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Diffuse Scattering of X-Rays from Sylvine. II

G. G. HARVEY,* *Ryerson Physical Laboratory, University of Chicago*
(Received February 16, 1933)

The absolute intensity of the diffuse scattering of x-rays of wave-length 0.71A from sylvine has been measured for a range of angles from 5° to 110°. Homogeneous radiation obtained by the use of balanced filters was used. Woo's formula taking account of the incoherence of part of the scattering was used to calculate the average atomic structure factors of the ions K^+ and Cl^-. The results are in good agreement with Wollan's values for argon as well as theoretical values calculated from a Schrödinger charge distribution by Hartree's method.

I. INTRODUCTION

IT has been shown[1,2] that the diffuse scattering from a simple cubic crystal consisting of atoms of one kind should be given classically by

$$S_{\text{class.}} = 1 + (Z-1)f'^2/Z^2 - F^2/Z, \qquad (1)$$

where $S_{\text{class.}}$ is the scattering per electron in terms of the Thomson[3] value in the same direction, Z the atomic number, F the atomic structure factor including the effect of thermal agitation and f' a quantity related to[1] the true atomic structure factor f. Woo[4] has independently deduced a similar formula, taking account of the fact that part of the scattering is incoherent. Woo's formula may be written

$$S = (f'^2 - F^2)/Z + (1 - f'^2/Z^2)(1 + \alpha \text{ vers } \phi)^3, \qquad (2)$$

where ϕ is the angle of scattering and $\alpha = h/mc\lambda$. The first term in Eq. (2) represents the coherent and the second the incoherent part of the scattering.

Several investigators[5,6,7,8,9] have reported measurements on the diffuse scattering of x-rays from crystals but in no case has homogeneous radiation been used. Although previous measurements on sylvine[7] gave values of the structure factors f' in good agreement with Wollan's values[10] for argon it was thought that this agreement was somewhat fortuitous in that no correction was made for incoherent radiation (Woo's paper[4] had not then appeared) and the wave-length range, though apparently narrow as measured by absorption, must have been rather broad. Further, it does not seem to the writer that an *average* wave-length as measured by absorption is the correct average to use for the

* National Research Fellow.

[1] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

[2] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931).

[3] J. J. Thomson, *Conduction of Electricity through Gases*, 2nd edition p. 325.

[4] Y. H. Woo, Phys. Rev. **38**, 6 (1931).

[5] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922).

[6] G. E. M. Jauncey and H. L. May, Phys. Rev. **23**, 128 (1924).

[7] G. G. Harvey, Phys. Rev. **38**, 593 (1931). The values of s_ϕ/ρ on p. 601 of this paper must all be multiplied by 0.024.

[8] G. E. M. Jauncey and P. S. Williams, Phys. Rev. **41**, 127 (1932).

[9] G. E. M. Jauncey and Paul Ehrenfest II, Phys. Rev. **42**, 907 (1932).

[10] E. O. Wollan, Phys. Rev. **37**, 862 (1931).

process of scattering. For if $\bar{\lambda}_a$ is the average wave-length as measured by absorption and $\bar{\lambda}_s$ the correct value to use for scattering and if $I(\lambda)$ is the spectral distribution then

$$e^{-\mu(\bar{\lambda}_a)t}\int_{\lambda_0}^{\infty} I(\lambda)d\lambda \approx \int_{\lambda_0}^{\infty} I(\lambda)e^{-\mu(\lambda)t}d\lambda$$

for some particular range of values of t and

$$S(\bar{\lambda}_s)\int_{\lambda_0}^{\infty} I(\lambda)d\lambda = \int_{\lambda_0}^{\infty} I(\lambda)S(\lambda)d\lambda,$$

where $\mu(\lambda)$ is the absorption coefficient of the substance used in determining $\bar{\lambda}_a$, λ_0 the minimum wave-length and S is given by Eq. (2). It is obvious that in general $\bar{\lambda}_a \neq \bar{\lambda}_s$, though of course they may not differ greatly if the spectrum is not too extended. It is to be noted, however, that $\bar{\lambda}_s$ will also depend on ϕ. Recently in the case of sodium fluoride Jauncey and Williams[8] have found it necessary to take account of the fact that part of the scattered radiation is incoherent and although this effect is smaller for sylvine it is not negligible. It was hence thought desirable to repeat the measurements on sylvine using homogeneous radiation obtained by the use of a balanced filter.[11]

II. Apparatus and Procedure

A diagram of the apparatus used is shown in Fig. 1. T is a molybdenum target x-ray tube immersed in transformer oil in a lead box A. The tube was operated at 30 m.a. at a potential of about 42.5 kv peak with full wave kenotron rectification. The x-rays left the box through a small celluloid window after passing through about 2 mm of oil. The primary beam was defined by the "slits" s_1 and s_2 consisting of small circular holes. s_3 served to eliminate scattering from the slit s_2 and was slightly larger than the x-ray beam. The angular width of the beam was about one degree. The balanced ZrO_2–SrO filter was placed in front of s_1 and the radiation scattered by the crystal C was measured by an ionization chamber and a Compton electrometer operating at a sensitivity of 5000 mm/volt. The ionization chamber was built of copper and fitted with thin celluloid windows the absorption in which was too small to be measured. All insulation was of amber. The chamber was 7.5 cm long and filled with krypton at a pressure of 57 cm of mercury N.T.P. This results in an absorption of 85 percent for the Mo $K\alpha$ lines. The use of such a small chamber not only greatly reduces the residual ionization due to cosmic radiation and α-particles but results in a rather low capacity electrometer system with a consequent high charge sensitivity. Further details on the construction of such ionization chambers have been given by Compton elsewhere.[12]

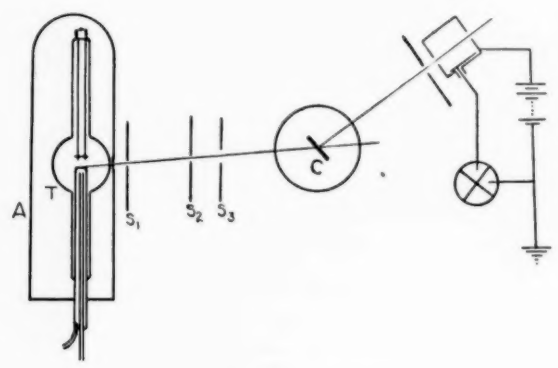

Fig. 1. Diagram of apparatus.

The transmission by the filters is shown in Fig. 2, the unshaded portion representing the part used. It is not to be supposed that this represents the energy distribution in the spectrum as no correction for absorption or second order reflection was made and a rather broad primary beam was used. This accounts for the peak at 0.8A and the very broad $K\alpha$ lines, though of course does not affect the correctness of the balance.

The procedure was the same as in previous experiments except that readings were taken with first one filter and then the other and the difference of the currents taken as a measure of the scattering for the Mo $K\alpha$ lines alone. Due to the fact that it is the difference of the readings that is required, it is necessary to take a large number of readings and in fact several thousand were taken. With the chamber set at an angle ϕ the ionization current was measured for a series of values of θ, the angle between the primary beam and the normal to the crystal face. At $\theta = \phi/2$ the Laue spot was not entirely absent as this would necessitate

[11] P. A. Ross, Phys. Rev. **28**, 425 (1926).

[12] A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931).

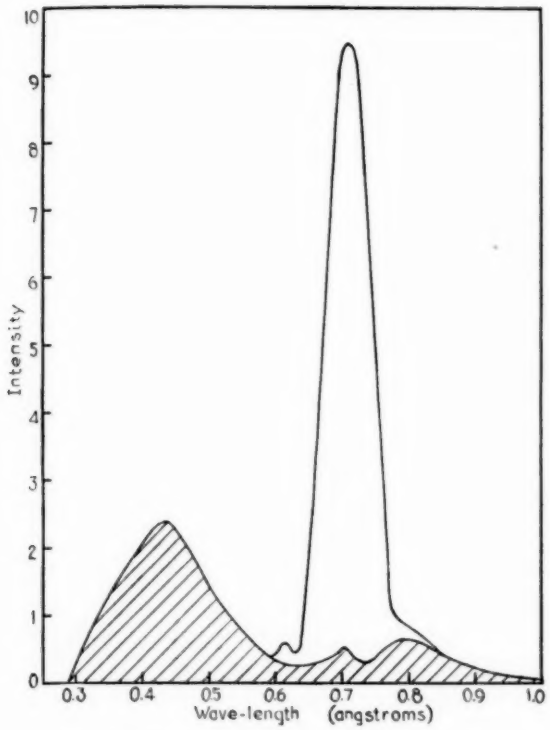

FIG. 2. Transmission by filters.

a more perfect balancing of the filters than is possible since the reflected and scattered intensities are of entirely different orders of magnitude. The Laue spot was never very intense, however (except of course for $\lambda = 0.71$A). The scattering from the crystal at an angle ϕ was then compared with that from a paraffin block at 90°. The ratio of the intensity transmitted by the crystal when set at $\theta = \phi/2$ to that transmitted by the paraffin at $\theta = 45°$ was also measured. Because of the rather high mass absorption coefficient of sylvine (13.7 cm^2 g^{-1}) it was necessary to use a very thin crystal, the surface density being 0.0843 g cm^{-2}. The surface density of the paraffin was 0.263 g cm^{-2}. The range of angles used extended from 5° to 110° and at the small angles it was necessary to correct for the height of the slit in front of the ionization chamber as it subtended an angle of about 5°.

It has been shown[13] that Crowther's formula[14] when modified to take account of the fact that part of the scattered radiation is incoherent because of the Compton effect, becomes

$$I_\phi = I_\phi' t(s_1 + s_2 T) \sec \phi/2, \qquad (3)$$

where I_ϕ is the scattered intensity per unit solid angle in the direction ϕ, I_ϕ' the transmitted intensity when the scattering block is set at $\theta = \phi/2$, t the thickness of the scattering block, s_1 and s_2 the spatial scattering coefficients for the unmodified and modified rays, respectively, and

$$T = (1 - e^{-(\mu' - \mu)t \sec \phi/2})/(\mu' - \mu)t \sec \phi/2, \qquad (4)$$

μ' and μ being the linear absorption coefficients for the modified and unmodified rays. In Eq. (4) we have neglected the difference in the absorption of the modified and unmodified rays in the air and ionization chamber window. Since the absorption in the ionization chamber is not complete account must be taken of the fact that the incoherent portion is more completely absorbed than the coherent. As the derivation of the required equation has been given by Jauncey and Williams[8] it will not be repeated here. Jauncey and Williams assumed all the radiation scattered by paraffin at 90° to be incoherent, since they used a rather short wave-length (0.39A). For 0.71A, however, the percentage of coherent scattering becomes appreciable and this introduces a slight modification. Their equation, thus modified, becomes

$$\frac{K_0(f'^2 - F^2)}{Z_e} + K_\phi T_c \frac{1 - f'^2/Z_c^2}{(1 + \alpha \text{ vers } \phi)^3} = \frac{K_0 A + K_{90} B T_P/(1+\alpha)^3}{1 + \cos^2 \phi} \left(\frac{W}{Z}\right)_C \left(\frac{Z}{W}\right)_P \left(\frac{C_\phi}{P_{90}}\right) \left(\frac{P}{C}\right), \qquad (5)$$

where K_ϕ is the percentage absorption in the ionization chamber for radiation of wave-length $0.71 + 0.024$ vers ϕ, C_ϕ the ionization current for scattering from the crystal at an angle ϕ, P_{90} the same for paraffin at 90°, C and P the currents produced by the rays transmitted by the crystal and paraffin, $(\rho t)_C$ the surface density of the crystal, $(\rho t)_P$ the same for paraffin, W and Z the atomic weights and atomic numbers, A and B the percentages of coherent and incoherent scattering from paraffin at 90°, and the other quanti-

[13] G. E. M. Jauncey and O. K. DeFoe, Phil. Mag. **1**, 711 (1926).

[14] J. A. Crowther, Proc. Roy. Soc. **A86**, 478 (1912).

ties have been previously defined. K_ϕ only varies from 0.85 to 0.88 from 0° to 110°.

To calculate the coherent scattering from paraffin Wentzel's formula[15] in the form given by Compton[16] was used in a previous[17] paper giving

$$I_{\text{coh.}} = 4I_e/(1+0.352\,x^2)^4, \qquad (6)$$

where I_e is the Thomson value of the scattering from a single electron and $x = (\sin\phi/2)/\lambda$, as the coherent intensity scattered by each carbon atom in paraffin, it being assumed that only the K electrons scatter coherently. Likewise for the incoherent intensity from the K electrons of a carbon atom we obtain

$$I_{\text{incoh.}} = 2I_e[1-1/(1+0.352x^2)^4]. \qquad (7)$$

Taking the formula for paraffin as C_nH_{2n+2} and assuming all the scattering from hydrogen to be incoherent we obtain for $\phi = 90°$

$$I_{\text{coh.}}/I_{\text{total}} = 1.2n/(7.4n+2) = 0.16 \qquad (8)$$

for all values of n above 20. Thus in Eq. (5), $A = 0.16$ and $B = 0.84$. Inserting the experimental values of C_ϕ/P_{90} and P/C in Eq. (5) and using values of F as given by James and Brindley[18] we may calculate values of f'. The structure factors so calculated are given in Table I. The values in parentheses are rather doubtful because of the extremely weak intensity. These values of f' are also plotted in Fig. 3. The solid curve represents the average of f_{K^+} and f_{Cl^-} as calculated by James and Brindley[19] from a Schrödinger charge distribution by the method of Hartree. The crosses represent Wollan's values [10] for argon calculated from Compton's formula for the scattering from a monatomic gas[16] and the circles represent the present values for sylvine. Although it was not possible with the wave-length used here to go out to as large values of $(\sin\phi/2)/\lambda$ as previously[7] there is an indication that the present values give better agreement with theory at large angles. It may be mentioned that the f values for argon as given by James and Brindley[19] are slightly larger than the average for K^+ and Cl^- at small values of x but slightly smaller for large x. It is seen from Fig. 3 that at small angles Wollan's values for argon are above those for sylvine, though the

TABLE I. *Structure factors.*

ϕ	x	F	f'	$S_{\text{class.}}$
5°	0.061	17.2	(17.2)	(0.06)
10	0.123	14.3	15.15	1.80
15	0.184	11.8	12.95	2.07
20	0.245	9.9	11.61	2.62
25	0.306	7.85	10.00	2.82
30	0.365	6.45	9.03	2.97
35	0.424	5.48	8.15	2.82
40	0.482	4.57	7.61	2.87
50	0.596	3.40	6.65	2.67
60	0.704	2.45	5.95	2.53
70	0.808	1.73	5.6	2.47
80	0.905	1.12	4.7	2.09
90	0.995	0.75	4.3	1.98
100	1.080	0.50	(3.6)	(1.67)
110	1.154	0.35	(3.25)	(1.55)

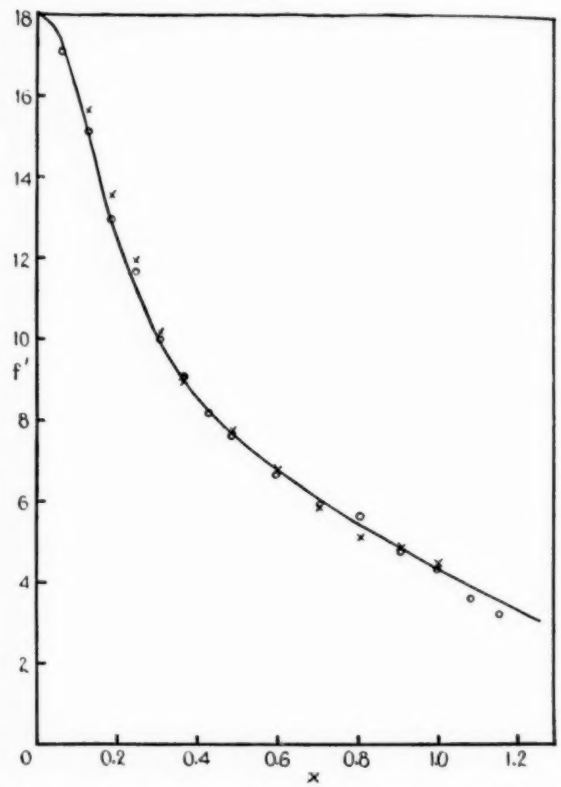

FIG. 3. Structure factors. Crosses, argon (Wollan); circles, sylvine; solid curve, $\frac{1}{2}(K^+ + Cl^-)$-wave mechanics.

[15] G. Wentzel, Zeits. f. Physik **43**, 1, 779 (1927).

[16] A. H. Compton, Phys. Rev. **35**, 925 (1930).

[17] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 698 (1931). In this paper the factor 2 was omitted in the exponential occurring in $u(r)$, Eq. (11), and the exponent 4 in the denominator of Eq. (12). The correct form was used in the calculations, however.

[18] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

[19] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

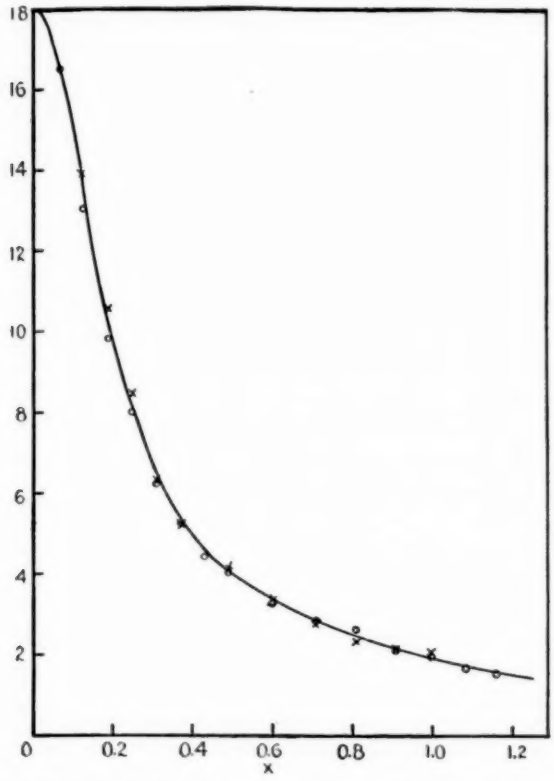

FIG. 4. Comparison with scattering from argon. Crosses $= S_{gas}$ (Wollan); circles $= (S+F^2/Z)_{crystal}$.

difference is perhaps within the combined experimental errors of the two sets of measurements. At large angles the difference is in the same direction but the intensity at large angles is extremely weak and this difference is less than the probable error of the sylvine measurements alone.

It has been pointed out[20] that the scattering from a crystal, reflection from a crystal, and scattering from a monatomic gas having the same atomic number as the crystal are related by the equation

$$S_{gas} = (S+F^2/Z)_{crystal}. \qquad (9)$$

This relation holds whether the S values are classical or modified to take account of the Compton effect but as Wollan's values are tabulated as $S_{class.}$ we shall use this form. The values of S in the last column of Table I were calculated from Eq. (1) with the f' and F values given there. In Fig. 4 values of $S_{class.}+F^2/Z$ for sylvine are indicated by circles and Wollan's values of $S_{class.}$ for argon by crosses. It is seen that the agreement is very good on the whole but, again, at small angles there is a small difference.

III. Conclusion

Data on the diffuse scattering from sylvine when combined with results on reflection yield values of the structure factors which within the limits of experimental error agree with those calculated from a Hartree model. The difference between the structure factors for argon and sylvine, though hardly significant, is in general in the right direction.

The primary purpose of this investigation was to determine the effect of temperature on the intensity of the diffuse scattering. Experiments at the temperature of liquid air with monochromatic radiation are now in progress and will be reported later.

In conclusion the author wishes to express his appreciation to Professor Arthur H. Compton for his interest in the work and for the use of the Ryerson Physical Laboratory.

[20] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1071 (1931).

Absolute X-Ray Reflectivities of Single Crystals of Calcite, Rocksalt, Rochelle Salt and Barite

PAUL KIRKPATRICK AND P. A. ROSS, *Stanford University*

(Received February 4, 1933)

With a two-crystal spectrometer absolute x-ray reflectivity measurements have been performed upon four different crystals. In the case of a large calcite crystal of uniform appearance, considered a good spectrometer crystal, with $K\alpha$ radiation of silver it is found that the theoretical values of percent reflection, integrated reflection, and rocking curve width calculated by Allison on the basis of the Darwin-Prins theory of reflection by a perfect absorbing crystal are not attained, the experimental and theoretical quantities being related by a factor not far from two in each case. Rocksalt crystals from a large exhibition specimen from Russia were found to be much more perfect in structure than any rocksalt specimens heretofore reported in the literature of x-ray spectrometry. Rocksalt reflectivity data for Ag $K\alpha$ are given. Artificial Rochelle salt crystals are found to possess rocking curve widths as narrow as those of high-grade calcite, indicating a very uniform structure; at the same time the reflections are relatively weak. Rochelle salt reflectivity data for Ag $K\alpha$ are given. Percent reflection, rocking curve width and integrated reflection of barite were determined for eleven wave-lengths, and scattering factors were calculated. The variation of the scattering factor with wave-length in the neighborhood of the barium K limit is similar to the variation previously found by Wyckoff and by Glocker and Schäfer for lighter elements except that Wyckoff's maximum does not appear.

IN relatively few cases have the x-ray reflecting characteristics of crystals received the direct attention of investigators. Calcite has been rather adequately studied on account of its great interest as a spectrometer crystal. Existing data upon rocksalt may be traced partly to a similar interest and partly to the importance of this crystal as a standard reflector for use in the analyses of other crystals. In the performance of such analyses spectrometer observations of intensities of reflection have of course been made on many crystals, but while these observations have been sufficient for their ends they are often of diminished permanent value in themselves either because of the slight attention paid to absolute as contrasted with relative values, or because the reflection data themselves do not attain publication. Since the integrated reflection is the only reflection characteristic of use to the crystal analyzer, his work at best provides no information about the angular distribution of reflecting power, nor can this characteristic be deduced in the general case from a knowledge of the crystal structure, however complete.

The reflectivity observations presented below were obtained with a two-crystal spectrometer which has been previously described.[1] The x-ray tube, a dismountable type with changeable targets, was operated on constant potential direct current and continuously evacuated by a strong pumping system. The reflectivity determinations discussed below were all conducted according to a uniform procedure which in its general aspects is familiar through the writings of Davis,[2] Allison[3] and others. Having selected the crystal to be examined, an entirely similar one in material, perfection, and treatment was mounted in the A position. The Seemann slit of the A crystal was adjusted to an opening of about half a millimeter. A narrow self-centering slit was mounted on the B crystal table, the crystal and its Seemann slit being absent, and the A crystal was adjusted in its holding device by screws provided for the purpose until radiation reflected from it was received centrally through the slit on the B table. This condition was sometimes observed by using the spectrometer ion chamber, but the adjustment

[1] P. A. Ross, R.S.I. **3**, 253 (1932).

[2] B. Davis and W. M. Stempel, Phys. Rev. **17**, 608 (1921); **19**, 504 (1922). B. Davis and H. M. Terrill, Phil. Mag. **45**, 463 (1923).

[3] S. K. Allison and J. H. Williams, Phys. Rev. **35**, 1476 (1930).

could be made more rapidly and quite as accurately by employing a fluoroscope. A vertical slit about a millimeter wide and a horizontal slit several millimeters high were installed between A and B, to limit the beam incident upon B to a roughly central area of the crystal. The adjusting slit was removed and the B crystal placed in the parallel position with its Seemann slit opened so wide as to be inoperative. The twice-reflected beam was found with the chamber, and adjustments, often laborious, to insure parallelism of the mean reflecting planes of the two crystals were carried out.

Parallel rocking curves were obtained by turning crystal B, step by step, through the reflecting position and observing the power of the twice-reflected beam at each step. Tube potentials were maintained at such values as to avoid the production of undesired high-order reflections. Before and/or after determining the rocking curve, crystal B was removed from its table and the power of the once-reflected beam observed.

From these data were derived, in the case of each crystal and wave-length, the integrated reflection R, the percent reflection P, and the half width w of the rocking curve at a height half way between the maximum and the level of the flat background.

Calcite

The two similar pairs of crystals used are considered equal to the best spectrometer calcites in this laboratory. One pair, $1A$–$1B$, has been polished on the reflecting surfaces while the other pair U_2–T_2, remains as split. First order reflection data for the $K\alpha$ radiation of silver were obtained and are listed in the first two rows of Table I.

Table I. *Reflection of Ag $K\alpha$ by calcite.*

	w(seconds)	P	$R\times10^5$ (radians)
Polished surface ($1A-1B$)	20.5	30.0	9.63
Split surface (U_2-T_2)	3.3	30.6	2.25
Perfect crystal (theoretical)	1.63	79	1.50

The theoretical values in the third row are those computed by S. K. Allison[4] on the basis of Darwin's theory of a perfect crystal as modified by Prins to take account of absorption. (The effect of the modification is very slight at this wave-length.) In common with most of the calcite crystals which have been studied heretofore the present data deviate from the predictions for perfect crystals in a sense which indicates some degree of mosaic structure. Evidently these crystals are similar in quality to Allison's pair designated II; they typify a high but not perfect grade of spectrometer calcite.

Perfect crystal predictions are of course not applicable to crystals which have been polished, whatever their former state of perfection. Polishing in this case had the usual effect of increasing the integrated reflection of the crystal at the expense of resolving power.

Rocksalt

The rocksalt crystals used were from a fifty pound block of high quality, originating in Russia. The surfaces used were chosen from a large number of freshly cloven pieces by visual inspection and rough spectrometer examination. Not all of the pieces derived from this block were internally clear and superficially plane but the two specimens selected for use had the uniform appearance of fine calcite. Hence our rocksalt data, like those on calcite above, are not to be taken as representative of typical crystals of their kind but as pertaining to the best obtainable. Results for first-order reflection of the wave-length of silver $K\alpha$ were as follows:

$$R=18.2\times10^{-5}; \qquad w=87''; \qquad P=17.7.$$

The narrowness of the rocking curve shows the crystal to be very much more nearly perfect than any rocksalt crystal heretofore reported, though the width is still more than 50 times as great as the value for a perfect rocksalt crystal according to Darwin's[5] treatment. The present value of 87″ may be compared with a value of 900″ obtained by Bragg, James and Bosanquet,[6] with about the same wave-length and with the 300″ of Davis and Stempel.[2]

Though much of the early x-ray spectrographic work was done with rocksalt crystals, it is not

[4] S. K. Allison, Phys. Rev. **41**, 1 (1932).

[5] A. H. Compton, *X-Rays and Electrons*, (1926), p. 140.

[6] Bragg, James and Bosanquet, Phil. Mag. **42**, 1 (1921).

highly regarded at the present time for such purposes, since advancing refinement in measurement has increased the demand for higher resolving powers. We think that the discovery of rocksalt crystals with resolving powers three and a half times as high as the previous best should do something to restore this crystal to favor in investigations where intensity rather than extreme resolution is the principal desideratum. While the resolution is by no means to be compared with that of good split calcite, the integrated reflection is eight times as great.

Rochelle Salt

The Rochelle salt surfaces used were adjacent portions of a large (001) face of an artificially-grown crystal from a laboratory supply house. The material is available in this way because of the interest in its piezoelectric properties. The face as received was a rectangle 17 cm long and 9 cm in breadth; it was sawed into three pieces, all large for spectrometer use.

Rochelle salt is a sodium-potassium tartrate with the formula $KNaC_4H_4O_6—4H_2O$. The structure, apparently, has not been determined. The grating space normal to the (001) planes was determined by observing with a single crystal the separation of the silver $K\alpha$ lines in the first and second orders and found to be 5.93A. Reflectivity determinations were made for both first and second order reflections of silver $K\alpha$ and the results are summarized in Table II.

Table II. *Reflection of Ag Kα by Rochelle salt.*

Order of reflection	w (seconds)	P	$R\times10^5$
First	3.5	6.3	0.25
Second	1.5	1	0.020

These data are notable for the extreme narrowness of the rocking curves, resembling those of the best calcite, together with the very low percent reflections and integrated reflections. According to Darwin's[5] theory of reflection by perfect crystals the angular region of perfect reflection, a quantity closely related to the width of the rocking curve, is given by

$$\Delta\theta_0 = nF\lambda^2e^2 \cot\theta/\pi mc^2, \qquad (1)$$

where n is the number of scattering units in unit volume, F is the structure amplitude corresponding to the same scattering unit, and the other symbols are of obvious interpretation. The only uncertainty in evaluating $\Delta\theta_0$ results from the uncertainty in F. Being in ignorance of the crystal structure, we can do no more than calculate an upper limit for F by adding the form factors[7] of the constituent atoms of the chemical formula previously given. Such a calculation for the second order reflection leads to the value 101, which is the value that F would have for the second order reflection if temperature disturbances of the atomic positions did not occur and if the atoms were so located in the unit cell that they all scattered in phase. Of course neither of these conditions is fulfilled and consequently, on both counts, a lower value of F is to be expected, but we shall use the value 101 provisionally in Eq. (1), and obtain therefrom $\Delta\theta_0 = 11.5\times10^{-6} = 2.37''$. Allison[8] shows that if the diffraction pattern of a single crystal is of the Darwin form the half width at half maximum of the parallel rocking curve should be $w = 0.60\Delta\theta_0$. The theoretical half width at half maximum under the assumption that $F=101$ is therefore $0.60\times2.37 = 1.4''$, in striking coincidental agreement with the experimental value, 1.5″. This agreement may be taken as an indication that the approach of the crystal to perfection is comparable to the approach of F to the limiting value assumed. The low percent reflections do not, however, favor the presumption of a high state of perfection, but indicate that the narrow rocking curves result from a crystal structure permitting only a low degree of cooperation among the many atoms contributing to the scattering. It is perhaps unprofitable to speculate further upon this situation until some information about the crystal structure can be obtained. In spite of the low reflecting powers observed these gigantic and inexpensive crystals with resolving powers comparable to those of calcite should not be entirely overlooked as possible spectrometer material for certain applications.

[7] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

[8] S. K. Allison, Phys. Rev. **38**, 203 (1931).

Barite

Natural crystals of barite ($BaSO_4$) from Felsoebanya, Hungary, with cleavage faces 3 by 4 cm were mounted on the spectrometer in such a way as to utilize face reflections from the (001) planes. The length of the unit cell normal to these planes is given by Wyckoff[9] as 7.17A. If this value be taken as d in Bragg's equation, it is found that no first order reflections occur, because of the complete interference of identical planes of half the above separation. The first reflection observed is therefore in the second order, and all barite reflections hereinafter discussed are properly specified by (002).

The principal point of interest in connection with this crystal concerns the K limit of the barium constituent which comes within the available x-ray range. As it was desirable to select wave-lengths within this range with entire freedom, the continuous spectra of tungsten and platinum were used as sources. The rocking curves obtained were not all as symmetrical as those obtained with good crystals such as calcite but bear more resemblance to the curves of rock-salt of average quality. On a few occasions singular excrescences appeared on the sides or feet of the curves, which could be traced to faulty areas on the crystal face and removed by installing horizontal slits or by moving the crystal. Table III presents the experimental results for the eleven wave-lengths investigated, together with data for one additional wave-length (0.71A) taken from the work of James and Wood.[10]

Table III. *Barite reflection data and structure factors.*

$\lambda(A)$	w (min.)	P	R (rad.)$\times 10^5$	F'
0.260	11.5	0.47	2.46	118
0.295	7.0	0.50	1.54	99
0.306	8.0	0.6	2.34	
0.317	10	0.5	2.44	
0.330	5.3	1.6	6.56	
0.350	8	1.8	10.1	109.8
0.365	6.0	1.9	9.54	108.4
0.434	6.0	1.5	8.99	114.7
0.505	6	1.75	8.20	116.7
0.574	6.5	1.7	7.32	118.2
0.645	5.0	1.7	5.98	114.4
0.71			6.63	125

[9] R. W. G. Wyckoff, *The Structure of Crystals* (1931), p. 289.

[10] R. W. James and W. A. Wood, Proc. Roy. Soc. **A109**, 598 (1925).

Apparently there are no significant variations of the rocking curve width with wave-length, and the discussion to follow concerns the values of the integrated reflection. These are plotted in Fig. 1.

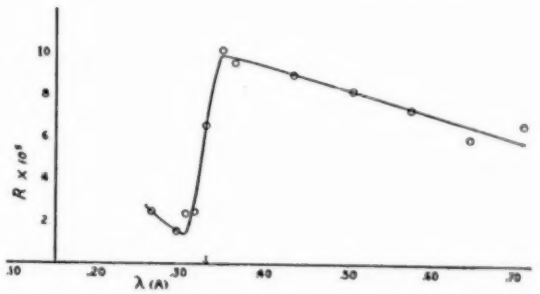

Fig. 1. Integrated (002) reflections of barite ($BaSO_4$). The last point, at the right is taken from James and Wood.[10]

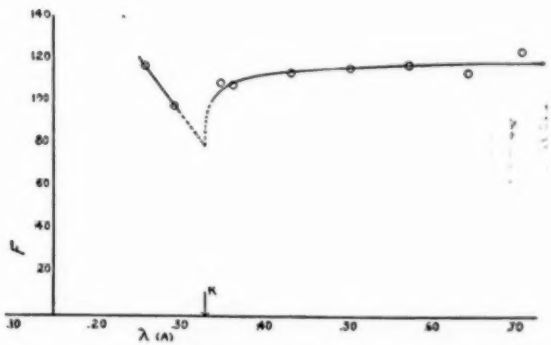

Fig. 2. Scattering factors of the barite unit cell (of four molecules) as derived from the integrated reflections of Fig. 1. (The three points of Fig. 1 nearest to the K limit do not permit the calculation of scattering factors because of uncertainty as to the appropriate absorption coefficients.)

The abrupt change which occurs at the wave-length of the barium K limit is most conspicuously displayed, though its full magnitude is not shown on account of the rounding effect of the finite wave band represented by each point. This break is chiefly caused by the change in absorption coefficient but a simple calculation shows that this change is insufficient to produce a discontinuity of the magnitude shown in the figure. A discontinuity in the scattering factor is indicated.

The last column of Table III and the curve of Fig. 2 exhibit the scattering factors of the unit cell, a group of four molecules, as computed by Darwin's[11] equation expressing the integrated

[11] R. W. G. Wyckoff, *The Structure of Crystals* (1931), p. 91.

reflection by imperfect crystals. This computation suffers from the usual uncertainties regarding the effects of extinction and of thermal agitation of the atoms, both of which effects have been ignored. Consequently on both counts we must expect the experimentally derived values of F to be too low, and this expectation is borne out by an independent calculation of the scattering factor of the unit cell, upon the basis of the independently known scattering factors of the constituent atoms and the structure of the barite crystal as determined by James and Wood.[10] In such a calculation no account is taken of the special effect of absorption limits; so the calculated result is to be compared with Fig. 2 only at the longest wave-lengths, where, apparently, the effect of the limit is no longer manifested. This calculation yields unit cell scattering factors from 150 to 157, depending upon which of several available lists of atomic scattering factors is adopted. These values are clearly in excess of anything which the curve of Fig. 2 could attain to.

If we are to succeed in separating the scattering factors of barium from those of the rest of the crystal it is necessary to consider the cause of this discrepancy. It is not practicable to correct our scattering factors for the effects of thermal movements in this crystal but it is known that the correction would affect all ordinates of the curve of Fig. 2 proportionally and therefore leave the shape of the curve unchanged. Primary extinction would have a like effect, but secondary extinction would alter the curve shape. Strong secondary extinction effects are judged to be improbable, however, in a crystal with such strong ordinary absorption, since the extinction coefficient affects the integrated reflection only as an additive term to an absorption coefficient already large. James and Wood studied the similar crystalline sulphates of barium, strontium and lead and found discrepancies between theoretical and observed integrated reflections of the wave-length 0.710A of just the kind encountered here. Had this difference been due to secondary extinction the discrepancy would presumably have been least in the strongly absorbent lead sulphate, whereas it was in fact greatest in this case. It seems correct to conclude that the shape of the curve representing the scattering factor of barium as a function of wave-length is as shown in Fig. 2, though the vertical scale of the plot is somewhat contracted and the constant scattering of the sulphur and oxygen atoms (about 55) has not been removed.

Variations of atomic scattering factors with wave-length, in the neighborhood of the K limits with the ratio $\sin\theta/\lambda$ held constant, have previously been measured by A. H. Armstrong[12] and by Wyckoff[13] for nickel and copper, and by Glocker and Schäfer,[14] and Bradley and Hope[15] for iron. The present measurements, though performed on an element with twice as many scattering electrons, are in good agreement with the earlier work in disclosing a minimum in scattering power at or near the wave-length of the limit. Our results however do not show any maximum value of the scattering factor on the long wave-length side of the limit, such as Wyckoff[16] described. In comparison with the predictions of the dispersion theory of Glocker and Shäfer our curve (Fig. 2) has the predicted general shape on the long wave-length side of the limit, but, like the experimental curve of Glocker and Shäfer, it rises too slowly on the side of shorter wave-lengths.

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[12] A. H. Armstrong, Phys. Rev. **34**, 931 (1929).

[13] R. W. G. Wyckoff, Phys. Rev. **36**, 1116 (1930).

[14] R. Glocker and K. Schäfer, Zeits. f. Physik **73**, 289 (1931).

[15] Bradley and Hope, Proc. Roy. Soc. **A136**, 272 (1932).

[16] The evidence upon which this maximum is claimed is not considered strong. The curve of Fig. 3 (Phys. Rev. **36**, 1120 (1930)), showing the maximum, is not in agreement with the accompanying data of Table IV, sloping down at the right of the maximum three or four times as rapidly as the tabulated data would permit. This curve shows the values of the (200) reflection of nickel. Values of the (111) reflection given in Table IV and not plotted give no evidence of a maximum.

The Cathodic Disintegration of Platinum by Mercury Ions

JOS. E. HENDERSON AND EDITH GIDEON, *University of Washington*

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The cathodic disintegration of platinum by mercury ions has been measured for ion velocities up to 2000 volts. The mercury ions were isolated into a beam and allowed to strike a platinum surface under such conditions that the secondary electron emission could be measured as well as the disintegration produced. The disintegration per positive ion was found to increase linearly with the energy of the ion up to 2000 volts. Approximately two atoms of platinum are ejected per incident ion of 1000 volts energy. Curves are shown which give the characteristics of the secondary electron emission as a function of the energy of the ion.

INTRODUCTION

THE phenomenon of cathodic disintegration, or sputtering as it is commonly designated, has been utilized by many laboratories for deposition of thin films of metal. Despite its wide use, the facts concerning the process are not well established. It is generally agreed that the phenomenon results from the stopping of fast moving positive ions by the cathode. There is considerable disagreement among investigators even as to the ease with which different ions and different materials sputter. Most of this disagreement arises from the manner in which the experiments are conducted. Nearly all experimenters[1] have used the material to be sputtered as the cathode of a glow discharge. Our lack of complete understanding of this type of discharge has therefore prevented an understanding of cathodic sputtering. The stopping of a positive ion is in general accompanied by the emission of electrons from the material struck. These electrons will constitute a portion of the current measured if the material to be sputtered is in the field accelerating the positive ions. The total number of positive ions taking part in such a sputtering process is therefore in doubt. Correction factors have been used[2] but, as the secondary electron emission is very much affected by surface conditions and history of the sample,[3] these estimates may be very much in error for the particular material sputtered. The purpose of the present experiment is to isolate a beam of positive ions and cause it to enter a chamber in which the secondary electron emission may be measured upon the particular sample being sputtered, or may be eliminated from the quantities measured. This permits a determination of the amount of material sputtered per positive ion and its variation with the velocity of the ion. Such a method encounters a considerable sacrifice in the magnitude of the quantities measured.

APPARATUS

A diagram of the apparatus will be found in Fig. 1. The tube is in two sections. The adjoining ends of the sections fit into grooves on opposite sides of the aluminum plate *A* and are sealed in position with Dennison's No. 2 hard sealing wax. A 14 mm opening through the aluminum plate joins the two sections. Across this opening is

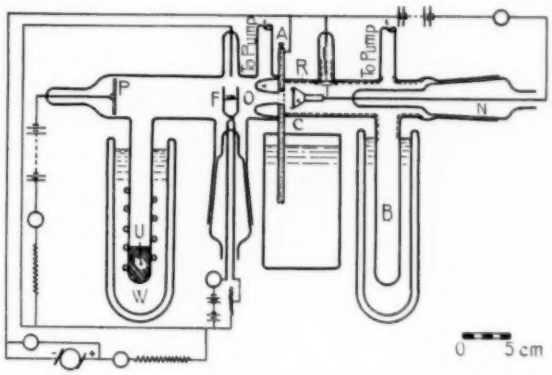

FIG. 1. Diagram of apparatus

[1] Compton and Langmuir, Rev. Mod. Phys. **2**, 186 (1930).

[2] Meyer and Guntherschulze, Zeits. f. Physik **71**, 279 (1931).

[3] Oliphant, Proc. Roy. Soc. **A127**, 373 (1930)

placed a grid of aluminum wire consisting of seven equally spaced parallel wires of 0.010 inch diameter. One section of the tube serves as the source of positive ions. The ions are obtained by ionizing mercury vapor between the filament F and the plate P which is of aluminum. The source of mercury vapor is the mercury in the side arm U. This mercury can be maintained at any desired temperature by a water-bath control. The mercury ions thus produced are accelerated through the grid across the opening in the aluminum plate into the section containing the plate C to be sputtered. The glass shield O serves to give some collimation to the positive ion beam.

This beam of positive ions is incident upon a platinum plate C, the supports of this plate being entirely of aluminum. Aluminum is used here and elsewhere because of its known low rate of sputtering. The entire inside surface of this section of the tube is covered with an opaque conducting layer of platinum R obtained by cathodic sputtering previous to assemblage. Contact to this layer is made by the platinum spring T. The platinum plate can be removed from the apparatus by means of the ground joint N. The arm B of the tube is immersed in liquid air to maintain the pressure in this portion of the tube as low as possible. Both sections of the apparatus are connected through liquid air traps to a vacuum system which includes a two-stage mercury diffusion pump.

Operation

The effective potential difference between the plate P and the filament F is between 75 and 80 volts. The plate A is maintained at arbitrary values from 400 to 2000 volts negative with respect to F by means of a direct-current motor generator. The platinum plate C, which is to be sputtered, is maintained at a potential of 100 volts positive with respect to A and R, to retain any electrons which might otherwise be emitted from C and thus be added to the reading of the positive ion current. Evidence that 100 volts is sufficient will be found in Fig. 2. This potential may be removed or reversed when it is desired to read the positive ion and secondary emission currents combined.

The water W, which controls the mercury temperature, is in general kept at about 57°C during the operation of the tube. In order to determine the order of magnitude of the effect due to the wax vapor, a run was made with the mercury U at room temperature. The pressure of the wax remained the same under these conditions, as the lower end of the plate A was still kept in cold water. The pressure of the mercury, however, decreased by a factor of fifteen. All currents were adjusted under these conditions to as nearly as possible the conditions which exist with the mercury at 57°C. The disintegration of the cathode then decreased to but 1/7 of the disintegration produced with the mercury pressure fifteen times as great, all other conditions remaining the same. We, therefore, conclude that the disintegration produced by positive ions of whatever constitutes the wax vapor is small compared to the effect produced by mercury ions. This is particularly true when it is considered that under the normal conditions of discharge the proportion of the positive ions of mercury to positive ions of wax vapor would be large. The effect of the wax vapor was to contribute to the magnitude of the positive ion current but not appreciably to the amount of material sputtered. Our values for the disintegration per positive ion may therefore be lower by a small amount than the true values.

The magnitude of the positive ion current striking the plate is kept approximately the same for the different accelerating voltages. The platinum plate, being mounted through a ground joint, is removed before and after each run, for weighing. The loss in weight (determined by

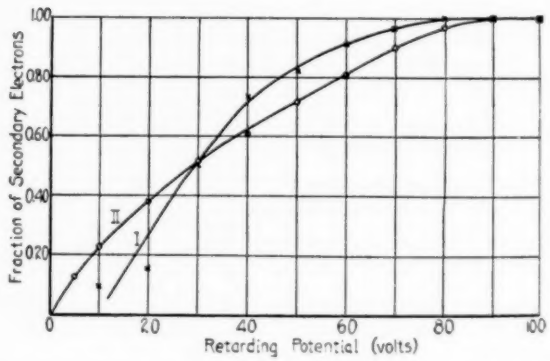

FIG. 2. Showing the fraction of the secondary electrons retained by the plate C for various retarding potentials. Curve I, 600 volt Hg ions; curve II, 2000 volt Hg ions.

means of a Becker micro-balance) is taken as the amount of material sputtered. The length of time the platinum plate undergoes bombardment is noted, and this quantity multiplied by the current gives the amount of charge and therefore the number of ions which have struck the plate. The ions are assumed to be singly charged.[4]

Discussion of Results

Since the secondary electrons escaping from the plate *C* contribute to the current measured by the galvanometer *Z*, the secondary electron emission could be determined by measuring the combined positive ion current and secondary electron current obtained with no potential or small accelerating potential for electrons applied between plate *C* and the walls of the surrounding chamber, and subtracting from this the current to plate *C* when sufficient retarding potential is applied to hold the electrons on the plate. Such a method neglects the emission from the walls due to reflected ions and metastable atoms impinging there, or to other causes. Under the conditions of normal incidence prevailing in this experiment the number of reflected ions should be small.[5] Experimental evidence, that electron emission from the walls due to any cause whatsoever is negligible, was found in the fact that changing from no potential to an accelerating potential of as much as one hundred volts did not result in a measurable change in current to the plate *C*. In Fig. 2 are shown curves giving the fraction of the secondary electrons retained by plate *C* for different retarding potentials applied between the platinum plate *C* and the inner surface of the tube. It will be noted that approximately 100 volts are necessary to hold the secondary emitted electrons on the platinum plate *C* for the highest velocity ions used. Two curves are shown, *viz.*, for 600 volts and 2000 volts. The intermediate voltage curves lie in the region between these two curves. The higher velocity ions result in a larger proportion of high velocity secondary electrons. Throughout the experiments on disintegration, 100 volts retarding potential was continuously applied so that the readings taken would represent a true positive ion current.

Fig. 3 shows the number of secondary electrons emitted from the platinum per incident mercury ion over the range of 600 to 2000 volts. The values range from 0.3 to 0.5 for the platinum surface utilized in this experiment. The plate *C*

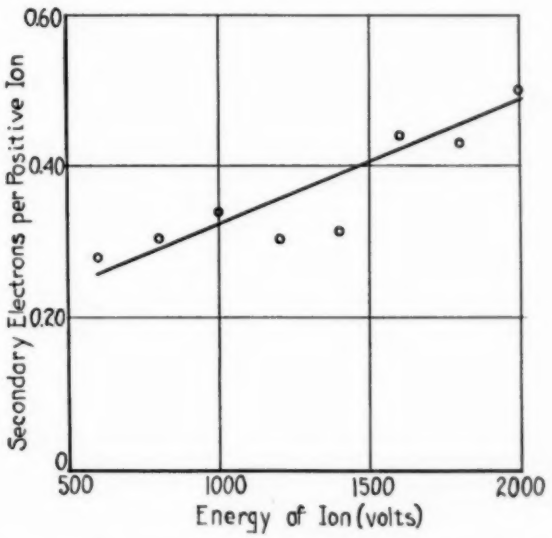

Fig. 3. The secondary electron emission from Pt per incident Hg ion for different energy ions. The platinum was removed from the apparatus between successive points.

was removed from the apparatus for weighing between the observations plotted in this curve. When this same curve was taken without removing the plate from the apparatus, a smooth straight line was obtained, justifying the curve drawn in Fig. 3. The deviation of the observed points from this curve illustrates well the type of variations observed for secondary electron emission, and shows the necessity of controlling the secondary electron emission in experiments of this character when extreme degassing of the parts is not possible. The characteristics of this curve are very similar to those observed by Oliphant[3] for helium ions incident upon cold molybdenum. The magnitude of the secondary electron emission observed shows the necessity for its consideration in determining the number of positive ions. The variation with energy of the ion makes essential the control of the secondary electron emission for experiments of the type under consideration.

[4] Bleakney, Phys. Rev. **35**, 139 (1930).
[5] Oliphant, Proc. Roy. Soc. **A132**, 631 (1931).

Curve 1, Fig. 4, shows the disintegration expressed in atoms sputtered per impacting positive ion and in grams per coulomb as a function of the energy of the positive ions. A straight line is considered by us to be the most representative of the trend of the points. The deviation of the points from this line we believe

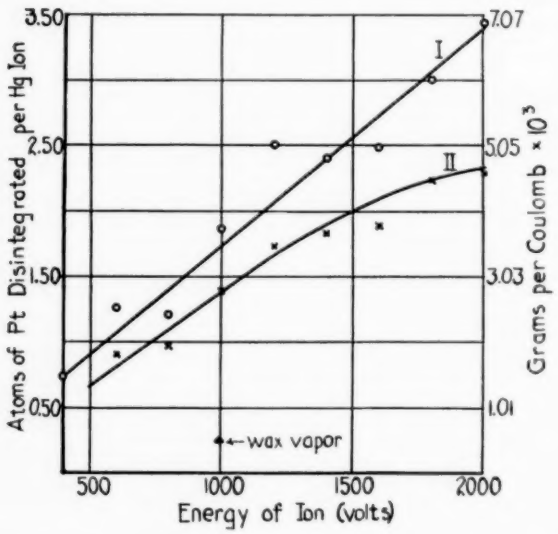

FIG. 4. The circles represent the number of atoms of platinum sputtered per impacting Hg ion. The crosses are the same data but neglecting secondary electron emission.

to be due to errors which resulted mainly from handling and weighing of the plate. This may be realized when one considers that the greatest loss of weight measured was of the order of 0.005 milligram. Disintegration by neutralized atoms which still possess velocity comparable to that of the impinging ions is a possibility which has been neglected in this experiment. Oliphant[6] gives evidence that disintegration by such atoms is far less intense than by positive ions with similar kinetic energy. Curve II is the one which would be obtained if the secondary electrons were permitted to contribute to the current measured. This curve is of the form obtained by other observers when the secondary electron emission is not controlled.[2, 7]

Although the materials used prevent a direct comparison with the work of other observers, the similarities found by them for different materials and different ions is strong evidence that the same laws govern for all materials. The results of these experiments show that up to 2000 volts, the disintegration is a linear function of the energy of the impacting ion. This strongly suggests that the sputtering process is not a direct transfer of momentum, but is more likely a process involving the energy directly such as might be expected from evaporation resulting from a local high temperature condition.

It is of interest to compute the efficiency of sputtering as a means for the evaporation of platinum. Taking the value of the disintegration at 1000 volts, the energy required to sputter one gram of platinum is 2.6×10^5 joules/gram. The energy required to heat and evaporate one gram of platinum at 4300°C is 3.3×10^3 joules/gram, giving as a means of evaporation of platinum an efficiency of a little more than one percent. The portion of the energy of the positive ion which is transformed into kinetic energy of the secondary electrons may be estimated from Fig. 2 and Fig. 3. For 1000 volt positive ions this is approximately one percent. This value for the secondary electron energy is undoubtedly higher than would have been obtained had it been possible thoroughly to degas the platinum. The sputtering and secondary electrons can thus account for from two to three percent of the energy of the positive ions. Of the remaining energy of the positive ion incident upon the metal at normal incidence the major portion is undoubtedly given up as heat. Evidence on this point is given by Oliphant,[4] who reports that, with helium ions incident upon nickel at normal incidence, the energy given up as heat is that possessed by the ion to within five percent over the range from 40 to 6000 volts.

[6] Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

[7] Von Hippel, Ann. d. Physik **81**, 1043 (1926).

The Polarizabilities of Ions from Spectra

JOSEPH E. MAYER AND MARIA GOEPPERT MAYER, *Chemical and Physical Laboratories, Johns Hopkins University*

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The polarizabilities of the gaseous alkali ions, and several other ions of rare gas structure, have been calculated by the Born-Heisenberg method from the corresponding spectra. Correction has been made for the effect due to "penetration" and for higher order distortion of the ion. The quantum mechanical derivation of the method has been given. The values of the polarizabilities of the alkali ions so obtained are found to be somewhat lower than those previously assumed. The polarizabilities of the gaseous negative ions must be correspondingly higher. The decrease in polarizability of the negative ion and increase of the positive ion on inclusion in a crystal is in agreement with known frequency shifts.

INTRODUCTION

THE sum of the polarizabilities of a negative and a positive ion in a crystal or in solution may be obtained by measurements of the dispersion. These sums indicate that the polarizability of a given ion is by no means independent of the state of the ion. It is different in solution and in crystal, and varies with the crystal. Fajans and Joos[1] have calculated values of the polarizabilities of the ions in the gaseous state, using reasonable but by no means certain assumptions. Pauling[2] by a semi-theoretical, semi-empirical method has calculated the polarizabilities of gaseous ions using the known polarizabilities of the corresponding rare gas and the assumed value of the negative ion. Since just the negative ions show polarizabilities extremely susceptible to the state, there is considerable doubt concerning their polarizabilities in the gaseous phase, and Pauling's method cannot be considered unimpeachable.

The only method of obtaining directly the polarizability in the gaseous state which may be called experimental, is that of Born and Heisenberg,[3] which uses the values of spectral terms. The actual calculations made by them (1924) are, however, by means of the Bohr model of the atom, which introduces considerable error. Great improvements have also been made since in the values and assignment of, spectral terms. Although the method is frequently referred to in the literature[4] it appears that no comprehensive attempt has been made to recalculate polarizabilities by this method using the quantum mechanics. Further, no quantum mechanical derivation of the fundamental equation of this method, Eq. (1) of this paper, appears to have been published. Whitelaw and Van Vleck[5] have reported the conditions under which the proof can be made, but their complete work has not been published. It has been thought desirable to make the proof and calculate some polarizabilities by this method. Throughout, the term values given in the new book by Bacher and Goudsmit[6] have been used.

METHOD

The principle of the Born and Heisenberg method is simple. Consider the energy of a spectral term with high quantum numbers n and l, of an alkali metal. The state of the valence electron may, to the zeroth approximation, be considered to be given by a hydrogen-like function which is assumed not to have appreciable amplitude inside of the ionic kernel. That is, the electron is assumed to be nonpenetrating. The poten-

[1] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

[2] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

[3] M. Born and W. Heisenberg, Zeits. f. Physik **23**, 407 (1924).

[4] An excellent discussion is given by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, page 215.

[5] N. G. Whitelaw and J. H. Van Vleck, Phys. Rev. **41**, 389, Abstract of Report to the New Haven meeting (1932).

[6] R. F. Bacher and S. Goudsmit, *Atomic Energy States*, McGraw-Hill, New York (1932).

tial on the electron is that due to the singly charged undeformed ionic kernel, plus a dipole perturbation potential due to the deformed ion, polarized under the influence of the valence electron. The zeroth order electrostatic potential of the undeformed ion would account for exactly the energy of a hydrogen state with the same quantum numbers. The perturbation method allows us to calculate the decrease of energy due to the polarization of the ion,

$$-\Delta E=\tfrac{1}{2}\alpha e^2(\overline{r^{-4}}). \tag{1}$$

In this equation $\overline{r^{-4}}$ is the average value of r^{-4} for the hydrogen state, that is,

$$\overline{r^{-4}}=\frac{\int r^{-2}|R_{n,\,l}(r)|^2dr}{\int r^2|R_{n,\,l}(r)|^2dr} \tag{2}$$

if $R_{n,\,l}(r)$ is the (unnormalized) radial hydrogen function with the quantum numbers n, l, of the term in question. By use of experimental deviations of term energies from those of hydrogen terms the polarizability α of the ion may be calculated. This is, of course, the polarizability of the ion under the influence of a field with the frequency of the atomic term in question. In all cases treated in this paper the frequency is so far below the resonance line of the ion that this correction is less than one percent.

The justification and details of the calculation will be given under the heading "Calculations." By this method the calculated polarizabilities for any single ion are found to vary considerably with the term used. In general the calculated polarizability is found to increase with the total quantum number n in a series of constant l, and to have lower values if a series of higher l is used in the calculation.

However, the values of α so calculated from the P and D terms of Li I, Be II, B III and C IV; the D and F terms of Na I, Mg II and Al III; and the F and G terms of K I, Rb I, Cs I, Ca II, Sr II, are sufficiently close to the probable values of α for the corresponding ions, and show a sufficient regularity in the trend to give hope that by considering second order effects reliable values may be obtained. Two corrections have then been made, a correction for the perturbation energy due to higher order distortion of the ion, and a correction due to penetration.

The effect on the energy due to higher than dipole distortion of the ion can be shown to be due to a constant of the ion which may be termed its "quadrupolarizability," the ratio of which to the "dipolarizability" can be estimated.

A further perturbation which is present even were the ion undistorted may be termed the penetration perturbation. If $Z(r)$, the effective nuclear charge at the radius r from the center of the ion, be defined as the net charge, in units of the charge on an electron e, lying within the radius r, then a perturbation potential at r exists $U_{\text{pen}}(r)$ defined by the equation

$$\frac{dU}{dr}=\frac{e^2(Z(r)-Z_\infty)}{r^2}.$$

Although $Z(r)$ has been calculated for many ions to obtain form factors which determine x-ray reflection intensities, values for only a few ions have been published. The values for Na^+, Cl^-, He and Rb^+ are found in an article by Hartree,[7] for Li^+, in an article by Hargreaves,[8] and a curve from which the values for K^+ may be obtained in an article by James and Brindley.[9] Some other curves of electron density obtained from experimental data have been published[10] but are of little value for the range of large radii which are here important. The authors are indebted to Professor J. C. Slater for a copy of a table of $Z(r)$ values for Cs^+, obtained by him from Hartree.

Graphical integration of the perturbation potential times ψ^2, which gives the perturbation energy, indicates that the perturbation at large radii alone is important ($r>1.5$ in units of $a_0=0.5285\times10^{-8}$ cm). For this portion of the ion an empirical analytical expression for $Z(r)$ may be obtained, the constants of which can be extrapolated for other ions.

The calculations are given in more detail under that heading. In Table I the results of the calcu-

[7] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1927).
[8] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1928).
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TABLE I.

Element, spectrum, and charge	Term	Term value T cm^{-1}	$T/Z^2-R/n^2=\Delta T_{exp}/Z^2$ cm^{-1}	$\Delta T_{pen}/Z^2$ cm^{-1}	$\Delta T_\alpha/Z^2$ cm^{-1}	$\alpha_0\times10^{24}$ cm^3	C_q	$\alpha\times10^{24}$ cm^3
Li	2*P*	28 582.5	1150.3	187.0	963.3	0.0310	?	
Sp. Li I	3*P*	12 560.4	368.4	73.2	295.2	0.0289	?	
$Z=1$	4*P*	7 018.2	160.1	32.2	127.9	0.0284	?	
	3*D*	12 203.1	11.1	0.5	10.6	0.0258	1.05	0.0246
	4*D*	6 863.5	5.4	0.2	5.2	0.0273	1.06	0.0258
	5*D*	4 389.6	0.5	0.0	0.5	0.005	1.07	
Be^{++}	2*P*	114 959.6	1302.4	279.0	1023.4	0.00825	?	
Sp. Be II	3*P*	50 384.4	402.4	73.0	329.4	0.00805	?	
$Z=2$	4*P*	28 122	172	33	139	0.00785	?	
	3*D*	48 828.5	14.8	1.0	13.8	0.00841	1.11	0.00756
	4*D*	27 459.5	6.7	0.9	5.8	0.00746	1.14	0.00656
	5*D*	17 570.4	3.4	0.5	2.9	0.00696	1.15	0.00605
B^{+++}	2*P*	257 555.5	1170	190	980	0.00340	?	
Sp. B III	3*P*	112 976.8	356	62	294	0.00320	?	
$Z=3$	4*P*	63 100.1	153	27	126	0.00312	?	
	3*D*	109 861.0	14.4	1.1	13.3	0.00361	1.16	0.00311
	4*D*	61 794.7	7.75	0.67	0.67	0.00405	1.20	0.00338
	5*D*	39 541.8	4.27	0.32	3.95	0.00421	1.21	0.00348
	4*F*	61 731.9	.87	0.00	0.87	0.0035	1.01	0.0035
C^{++++}	2*P*	435 637.9	919	153	766	0.00154	?	
Sp. C IV	3*P*	200 110.4	314	48	266	0.00162	?	
$Z=4$	4*P*	111 858.7	133	22	111	0.00155	?	
	3*D*	195 292	13.2	1.1	12.1	0.00185	1.20	0.00154
	4*D*	109 837.6	6.6	0.6	6.0	0.00193	1.25	0.00154
	5*D*	70 286.5	3.6	0.3	3.3	0.00198	1.26	0.00157
	4*F*	109 743.7	0.7	0.0	0.7	0.00157	1.02	0.00154
Na^+	3*D*	12 276.18	83.45	8.13	75.32	0.184	1.11	0.165
Sp. Na I	4*D*	6 900.35	41.94	4.66	37.28	0.192	1.13	0.170
$Z=1$	5*D*	4 412.47	23.09	2.82	20.27	0.194	1.14	0.170
	4*F*	6 860.37	1.96	0.02	1.95	0.070	1.01	0.069
	5*F*	4 390.37	0.99	0.01	0.98	0.062	1.01	0.061
Mg^{++}	3*D*	49 777.0	251.5	31.5	220.0	0.134	1.27	0.105
Sp. Mg II	4*D*	27 955.3	130.4	18.0	112.4	0.144	1.34	0.107
$Z=2$	5*D*	17 846.3	72.2	11.2	61.0	0.146	1.36	0.107
	4*F*	27 467.4	8.43	0.17	8.26	0.074	1.03	0.072
	5*F*	17 577.2	4.92	0.14	4.78	0.076	1.03	0.074
	6*F*	12 204.8	3.02	0.12	2.90	0.074	1.03	0.072
Al^{+++}	3*D*	113 497.9	418	46.5	371.5	0.100	1.47	0.069
Sp. Al III	4*F*	61 841.7	12.89	0.39	12.50	0.050	1.05	0.047
$Z=3$	5*F*	39 578.6	8.24	0.31	7.93	0.056	1.06	0.053
	6*F*	27 484.5	5.64	0.23	5.41	0.061	1.06	0.058
	5*G*	39 526.2	2.41	0.01	2.40	0.070	1.00	0.070
K^+	4*F*	6 878.5	20.0	0.14	19.9	0.715	1.03	0.694
Sp. K I	5*F*	4 404.2	14.8	0.1	14.7	0.925	1.04	0.890
$Z=1$	6*F*	3 056.5	8.3	0.1	8.2	0.840	1.04	0.807
Ca^{++}	4*F*	27 694.0	65.0	1.5	63.5	0.571	1.06	0.540
Sp. Ca II	5*F*	17 714.1	39.1	1.2	37.9	0.600	1.08	0.555
$Z=2$	6*F*	12 290.0	24.3	0.9	23.4	0.600	1.09	0.550
	6*G*	12 211.0	4.54	0.0	4.54	0.46	1.01	0.46
Rb^+	4*F*	6 987.6	39.0	1.0	38.0	1.37	1.05	1.30
Sp. Rb I	5*F*	4 418.2	28.7	0.8	27.9	1.77	1.06	1.66
$Z=1$	6*F*	3 068.0	19.7	0.6	19.1	1.95	1.07	1.83
Sr^{++}	4*F*	27 960.4	131.5	8.6	122.9	1.10	1.15	0.96
Sp. Sr II	5*F*	17 896	84	7.0	77	1.22	1.19	1.02
$Z=2$	6*F*	12 412	55	5	50	1.28	1.21	1.06
Cs^+	4*F*	6 932.80	74.27	2.73	71.54	2.58	1.07	2.38
Sp. Cs I	5*F*	4 433.00	43.55	2.26	41.29	2.61	1.09	2.39
$Z=1$	6*F*	3 074.77	26.54	1.58	24.96	2.56	1.10	2.33
	5*G*	4 393.5	4.05	0.01	4.06	1.1	1.02	1.1
	6*G*	3 057.0	8.77	0.01	8.76	3.6	1.02	3.5

lation are given. The method is to subtract the experimental term value T divided by Z^2 from the hydrogenic value, R/n_0^2. This difference is given in column 4. The part of this, $\Delta T_{\text{pen}}/Z^2$, calculated as due to penetration, tabulated in column 5, is subtracted, leaving $\Delta T_\alpha/Z^2$ (column 6). This $\Delta T_\alpha/Z^2$ is the term defect, divided by the ionic charge squared, due to distortion of the ion. From this α_0, the polarizability, is calculated, (column 7) without consideration of the effect due to the quadropolarizability. The effect of the higher distortion is then taken into account by dividing by a factor C_q, the expression for which is given in Eq. (14) and which is tabulated in column 8. In column 9 the final value of the polarizability α is given.

Calculations

(a). The deformation effect

The complete zeroth order function Ψ_k of the atom, neglecting interaction between the ionic kernel and the valence electron is written as a product of the ionic function $\psi_m{}^i$ with the quantum numbers m, and a hydrogen-like function $\psi_p{}^v$ for the valence electron. p is an abbreviation for the quantum numbers n, l, and the orientation quantum number m_l. We wish to calculate the perturbation of a state $k=0 (m=0,\ p=p_0)$.

$$\Psi_k=\psi_m{}^i\psi_p{}^v, \quad \Psi_0=\psi_0{}^i\psi_{p_0}{}^v, \quad \overset{0}{E}_k=\overset{0}{E}_m{}^i+\overset{0}{E}_p{}^v. \tag{3}$$

The perturbation potential H due to the distortion of the kernel may be written

$$H=H^a+H^b \qquad \text{with} \qquad H^a=-e^2\frac{\mathbf{R}\cdot\mathbf{r}}{r^3}, \qquad H^b=-\frac{1}{2}e^2\frac{1}{r^3}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2-R^2\right], \tag{4}$$

$$\mathbf{R}=\sum_i\mathbf{r}_i, \qquad R=|\mathbf{R}|$$

in which $\mathbf{r}$ and $\mathbf{R}$ designate the vector radii of the valence electron and the ion, respectively. Correctly $\mathbf{R}$ is a sum over the vector radii $\mathbf{r}_i$ of all of the electrons i in the kernel. r and R are the respective magnitudes. H^a is the dipole, H^b the quadrupole distortion.

If we define H_{0k} by the equations,

$$H_{0k}=H_{0k}{}^a+H_{0k}{}^b, \qquad H_{0k}{}^a=\int\overline{\Psi}_0H^a\Psi_k d\tau, \qquad H_{0k}{}^b=\int\overline{\Psi}_0H^b\Psi_k d\tau, \tag{5}$$

all products $H_{0k}{}^a\times H_{k0}{}^b$ as well as the first order energy H_{00} are zero because of the form of H. Further, the degeneracy in the orientation quantum number m_l of the hydrogen state is not lifted by the perturbation, and the states of different l are the correct zeroth order approximations to the problem. Applying the conventional method of the perturbation theory, one obtains

$$\Delta E_0=\Delta E_0{}^{(2)}=\sum_{mp}\left[|(H^a{}_{0p_0,\ mp}|^2+|H^b{}_{0p_0,\ mp}|^2)/(\overset{0}{E}_0-\overset{0}{E}_m{}^i-\overset{0}{E}_p{}^v)\right]. \tag{6}$$

The energy term $\overset{0}{E}_p{}^v$ which is small compared to $\overset{0}{E}_0-\overset{0}{E}_m{}^i$ is neglected. (The term $m=0$ does not occur in this sum.) The sums over p are then evaluated by observing that

$$\begin{aligned}\sum_p|H^a{}_{0p_0,\ mp}|^2+|H^b{}_{0p_0,\ mp}|^2&=-e^4\sum_p\left|\left\{\mathbf{R}_{0m}\cdot\left(\frac{\mathbf{r}}{r^3}\right)\right\}_{p_0,\ p}\right|^2+\frac{1}{4}\left|\left\{\frac{1}{r^3}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2_{0m}-R_{0m}\right]\right\}_{p_0,\ p}\right|^2\\ &=-e^4\left\{\left(\mathbf{R}_{0m}\cdot\frac{\mathbf{r}}{r^3}\right)^2+\frac{1}{4r^6}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2_{0m}-R_{0m}{}^2\right]^2\right\}_{p_0p_0}=-\frac{e^4}{3}\left[|R_{0m}|^2(r^{-4})_{p_0p_0}+\frac{3}{5}|R_{0m}{}^2|^2(r^{-6})_{p_0p_0}\right].\end{aligned} \tag{7}$$

The complete expressions for the change of energy due to deformation becomes

$$-\Delta E=(e^4/3)\{(r^{-4})_{p_0p_0}\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]+\tfrac{2}{5}(r^{-6})_{p_0p_0}\sum_m[|R_{0m}{}^2|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\}. \quad (8)$$

The polarizability α of the ion is given by

$$\alpha=\tfrac{2}{3}e^2\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]. \quad (9)$$

It is now desirable to obtain an approximate value for the second sum in Eq. (8) in terms of the polarizability. A customary approximation is to assume that all the significant terms in Eq. (9) occur at approximately the same energy, obtaining,

$$\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\cong R_{00}{}^2/E_a, \quad (10)$$

in which E_a is some average energy, approximately the ionization energy. A similar approximation leads to the equation,

$$\sum_m[|R_{0m}{}^2|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\cong\frac{R_{00}{}^4}{E_q}\cong\frac{(R_{00}{}^2)^2}{NE_a}\cong\frac{R_{00}{}^2}{N}\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)], \quad (11)$$

in which N is the number of outer electrons. The approximation (11) has been obtained in the following manner, both $R_{00}{}^2$ and $R_{00}{}^4$ are the sums of the average of these functions of r for the individual electrons i of the ion in its normal state. That is,

$$R_{00}{}^2=\sum_i(r_{00}{}^2)_i, \qquad R_{00}{}^4=\sum_i(r_{00}{}^4)_i. \quad (12)$$

There are N outer electrons of the ion whose individual $r_{00}{}^2$ and $r_{00}{}^4$ will be about equal, and these functions of all other (inner) electrons will be negligible. $r_{00}{}^4$ will be about equal to, and somewhat larger than, the square of $r_{00}{}^2$, making $R_{00}{}^4\cong(R_{00}{}^2)^2/N$. Further the average energy E_q will be somewhat larger than E_a. Numerically the values $N=8$ (and 2 for Li^+) have been chosen in making the arithmetical calculations.

Substituting (9) and (11) in (8) one obtains for the change in energy,

$$-\Delta E=\frac{1}{2}\alpha e^2(r^{-4})_{p_0p_0}\left[1+\frac{3}{5}\frac{R_{00}{}^2}{N}\frac{(r^{-6})_{p_0p_0}}{(r^{-4})_{p_0p_0}}\right]. \quad (13)$$

The unperturbed energy is that of a hydrogen like state, $-\overset{0}{E}=Rhc/n_0{}^2$, and the term value T is the negative of the energy divided by hc. One may then write the equation for α,

$$\alpha=\frac{2(R/n_0{}^2-T_{p_0})hc}{e^2(r^{-4})_{p_0p_0}[1+3R_{00}{}^2(r^{-6})_{p_0p_0}/5N(r^{-4})_{p_0p_0}]}=B_{p_0}Z_\infty{}^{-4}C_q{}^{-1}[R/n_0{}^2-T_{p_0}], \quad (14)$$

$$B_{p_0}Z_\infty{}^{-4}=\frac{2hc}{e^2}(r^{-4})_{p_0p_0}{}^{-1}, \qquad C_q=[1+3R_{00}{}^2(r^{-6})_{p_0p_0}/5N(r^{-4})_{p_0p_0}].$$

The values of $(r^{-4})_{p_0p_0}$ and of $(r^{-6})_{p_0p_0}$ may be easily evaluated knowing the hydrogen radial functions. Waller[11] has given an expression for $(r^{-4})_{p_0p_0}$. $R_{00}{}^2$ is connected with the specific magnetic susceptibility χ by the equation

$$R_{00}{}^2=(6m_0c^2/Ne^2)\chi. \quad (15)$$

The values of χ used are the experimental values tabulated by Pauling,[12] except for the first row of the periodic system, for which Pauling's theoretical values are used. The bracket in the denominator of Eq. (15), which is abbreviated as C_q, the correction for higher distortions is tabulated in Table I, column 8. $(r^{-6})_{p_0p_0}$ is divergent for P states and the correction cannot be made. This merely means that the P orbits

[11] I. Waller, Zeits. f. Physik **38**, 635 (1926).

[12] L. Pauling, Phys. Rev. **34**, 954 (1929).

penetrate the ion too strongly for this method of approximation.

(b). The penetration effect

Instead of using the difference between the experimental term value T and the hydrogen-like term value in the numerator of Eq. (15) the change in T, ΔT_{pen}, due to penetration has been subtracted. This effect is due to the deviation in the true potential from the assumed zeroth approximation due to the *undistorted* ionic kernel and may be handled independently of the distortion effects.

If $Z(r)$ is the effective nuclear charge as a function of r and Z_∞ the charge on the ion, the perturbation potential may be written.

$$dU/dr = e^2(Z(r)-Z_\infty)/r^2,$$
$$-U = e^2\left[\frac{Z(r)-Z_\infty}{r} - \int_r^\infty \frac{1}{r}\frac{dZ(r)}{dr}\,dr\right]. \tag{16}$$

The first order effect on the term value alone is considered.

$$\Delta T = -\frac{\Delta E}{hc} = -\frac{e^2}{hc}\int \bar{\psi}_{p_0}{}^v U \psi_{p_0}{}^v d\tau, \tag{17}$$

$Z(r)-Z_\infty$ is assumed to have the analytical form $\beta b r^2 e^{-\beta r}$, in which case $U(r)$ will have the form $U(r) = -(e^2 b/a_0)e^{-\beta r}$, when r is measured in units of a_0, the radius of the first Bohr orbit of hydrogen, ($a_0 = 0.5285\times10^{-8}$ cm.). This empirical equation for $Z(r)$ can be made to fit all the given tables of $Z(r)$ for large values of r by the proper choice of the constants b and β. Since the whole effect is at large r values it is unimportant that the equation is absolutely false for small r. No tables were at hand for the multiply charged ions. It was assumed that the equation $\beta = 2Z_e/n$ was approximately true with n the total quantum number of the outer electrons of the ion, and Z_e the effective charge on the electrons. Z_e was then assumed to increase by one as the charge on the ion increased by one, for the same configuration. In Table II are given the assumed values of b and β for the various ions. A few graphical integrations showed that the total penetration effect occurred in the region where the assumed form of the function $Z(r)$ was in agreement with the tabulated values.

TABLE II. *Empirical constants of the penetration potential.*

Ion	Li^+	Be^{++}	B^{+++}	C^{++++}	Na^+	Mg^{++}	Al^{+++}	K^+	Ca^{++}	Rb^+	Sr^{++}	Cs^+
b	9.5	9.5	9.5	9.5	33	33	33	34	34	35	35	36
β	5.43	7.43	9.43	11.43	4.05	5.05	6.05	3.09	3.76	2.42	2.92	2.11

RESULTS

In Table III are given the most probable values of α, as deduced only from the internal evidence of this calculation. Values previously published in the literature are included for comparison. The values for the rare gases are experimental, and quite accurate. They are copied from Pauling's tables.

Some considerations lead to misgivings about the accuracy of the values here computed. The consistently lower values of α obtained from a higher series in comparison with a lower series, F compared with D in sodium for instance, indicates some sort of systematic error. This may be a gross underestimation of the quadrupolariza-

TABLE III. *Polarizabilities of the gaseous ions.* ($\alpha\times10^{24}$ in cm^3.)

Ion	This paper	Pauling	Fajans and Joos	Born and Heisenberg ($k=l+\frac{1}{2}$)
He		0.204		
Li^+	0.025	0.0295	0.079	0.075
Be^{++}	0.007	0.0080	0.039	
B^{+++}	0.0033	0.00303		
C^{++++}	0.0015	0.00135		
Ne		0.396		
Na^+	0.17	0.182	0.197	0.21
Mg^{++}	0.10	0.092	0.110	0.12
Al^{+++}	0.53	0.054		0.065
Ar		1.645		
K^+	0.80	0.844	0.879	0.87
Ca^{++}	0.54	0.474	0.447	
Kr		2.49		
Rb^+	1.5 (?)	1.42	1.485	1.81
Sr^{++}	1.0	0.87	0.883	1.42
Xe		4.05		
Cs^+	2.35	2.45	2.577	2.79

bility correction, which is not unlikely since our approximation gives a lower limit to this correction, or a gross underestimation of the penetration effect which is less likely. Any such explanation would tend to give more weight to the values obtained from the higher series, indeed the true value would then be slightly less than that of the higher series, which seems unreasonable in the case of sodium at least.

For some ions an error may be introduced by a false estimation of the series limit. That is, although the differences in term values are well known, the absolute values are uncertain. That such uncertainties exist is apparent. Bacher and Goudsmit and the *International Critical Tables* differ by 2.6 cm^{-1} in the case of K I, and 98 cm^{-1} in Sr II. However the term values of Na I are probably known with great accuracy.

The results of this paper agree quite well with the calculations of Pauling. It is particularly to be noted that the agreement for the ions of the elements of the first row of the Periodic Table lends great support to Pauling's method, which for these ions is purely theoretical and assumes no empirical constants.

For most of the singly charged positive ions, (alkalis), the polarizabilities appear to be slightly lower than Pauling's values, and considerably lower than those of Fajans and Joos. Pauling has obtained the values which he gives by assuming a linear extrapolation of a screening constant, calculated from the polarizabilities of the corresponding rare gas atom and negative halide ion. If the deviation above noted is real, it would lead to the conclusion that the polarizabilities of the gaseous negative ions are greater, and indeed considerably greater, than those assumed by Pauling. This means that the gaseous negative ions have considerably higher polarizabilities than the same ions in crystals, and the gaseous positive ions somewhat lower α's than in the crystals.

TABLE IV.

Term	$2P$	$3P$	$4P$	$3D$	$4D$	$5D$	$4F$	$5F$	$6F$	$5G$	$6G$	$6H$
$B_{n_0l_0}\times 10^4$	0.322	0.978	2.228	24.4	51.5	96.0	360	634	1025	2640	4080	12850

If the approximation of Eq. (10) is used, leading to

$$\alpha \leqq \tfrac{2}{3}e^2(R_{00}^2/E_\alpha), \tag{18}$$

it might be assumed that R_{00}^2 is approximately independent of the state of any given ion and that the polarizability α varies inversely with the "main frequency." The absorption frequencies of negative ions in a crystal are more than double the probable absorption frequencies (near the electron affinity), in the gaseous state. The absorption frequencies of the positive ions, on the other hand, are probably lowered by inclusion in a crystal. It seems then, qualitatively, probable that the polarizabilities of positive ions are increased somewhat in passing from the gaseous into the crystalline (or aqueous) state, while those of the negative ions are enormously (twofold?) decreased by the same change of state.

For convenience the values of $B_{n_0l_0}$ of Eq. (14) are included in Table IV for different terms.

In conclusion the authors with to thank Professors M. Born and K. F. Herzfeld for helpful suggestions and criticism.

Effects of Chemical Combination on the X-Ray Emission Spectrum of Sulphur

JOSEPH VALASEK, *University of Minnesota*

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With an improved method to eliminate the effects of chemical reactions with the target material, the wave-lengths of the sulphur $K\alpha$ and β-lines were measured for the following substances: S, FeS, CoS, NiS, Cu_2S and ZnS. The superiority of the new technique over that usually employed is particularly evident in the spectrum of ZnS in which the $K\beta$-line is observed as a triplet instead of the single broad line heretofore observed. This result is independent of the target material. The $K\beta$-lines of CoS and NiS are observed for the first time. Two crystal modifications of ZnS, namely, zincblende and wurtzite, gave spectra which showed no appreciable differences.

THE first observations showing that the x-ray emission spectrum of an element depends on chemical combination were made in 1924 by Lindh and Lundquist. The effect is very small except in the case of the lighter elements, such as silicon, phosphorus, sulphur and chlorine. A summary of the work up to 1928 may be found in Lindh's book on *Roentgenspektroskopie*. Recent studies of the subject are those due to Lundquist,[1] Faessler,[2] Deodhar[3] and Svensson.[4] Deodhar, in particular, finds several new lines which are emitted by some compounds and not by others, indicating the creation of new energy levels in an atom when it is combined with one or more other atoms. In addition to this appearance of more or less characteristic lines, there are often shifts of a few X-units in the wave-lengths of some of the lines.

Although sulphur compounds have been investigated several times, in all but one of these studies,[2] and that one restricted to the intense α_1 and α_2-lines, the spectrum was excited by direct electron impact on the powdered compound. This was rubbed into scratches on the face of the target. What happens to the compound under these conditions is only now beginning to be clearly understood.[4] The chemical reaction between the substance and the target is evident from the fact that the "same" substance often gives a different spectrum depending on the underlying target metal.

In order to overcome such effects it has been often suggested that the spectrum of the compound should be excited by fluorescence instead of electron impact. This is the procedure followed by Faessler, who used one of the new type of x-ray tubes developed by Coster and Hevesy. In this form of tube, the powdered material is rubbed on a flattened portion of the electron focussing shield which surrounds the filament. However, Faessler's work covers only the intense α_1 and α_2-lines of sulphur, presumably because the other lines could not be obtained with sufficient intensity.

In order to study the less intense lines, particularly the β-lines which show the greatest dependence on chemical combination, the writer has used the target illustrated in Fig. 1. The substance S is protected from the direct impact of the electron stream by the copper shield C. The focal spot is one to two millimeters from the front of the material. This does not give a pure fluorescence spectrum, for many of the electrons no doubt are scattered from the target to the substance. However, the opportunity for chemical reaction is greatly reduced as the results

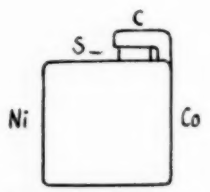

FIG. 1. X-ray target.

[1] Lundquist, Zeits. f. Physik **60**, 642 (1930).
[2] Faessler, Zeits. f. Physik **72**, 734 (1931).
[3] Deodhar, Proc. Roy. Soc. **A131**, 647 (1931).
[4] Svensson, Zeits. f. Physik **75**, 120 (1932).

show. The spectrum is of fair intensity. The usual exposure for the β-lines was 8 to 10 hours at 10 to 15 milliamperes and 12 to 15 kilovolts. In the case of pure sulphur, the current was reduced to 1 to 2 milliamperes to keep the sulphur from melting and running out onto the target.

A vacuum spectrograph of the Siegbahn type was employed. The crystal was of calcite, the wave-lengths being measured with the aid of comparison spectra. For the sulphur $K\alpha$-lines, cobalt $K\alpha_1$ was used in the third order, while for the $K\beta$-lines nickel $K\alpha_1$ was employed. These lines have been measured with ample accuracy by Eriksson.[5] The Bragg angles for these lines, with Larsson's value for the lattice constant of calcite in the third order,[6] are, at 18°C:

$$\text{Ni } K\alpha_1\ 55°\ 0'\ 25'' \qquad \text{Co } K\alpha_1\ 62°\ 7'\ 35''.$$

The angular separations between the reference lines and the sulphur lines were calculated from the distances along the plate as measured by a Gaertner comparator and the radius of the camera measured in the manner outlined by Lindh.[7] Temperature differences between the sulphur and comparison exposures were corrected for by the equation $\Delta\theta = 2.10'' \Delta T \tan\theta$. From the glancing angles so found, the wave-lengths of the sulphur lines were calculated with the aid of Larsson's value of the lattice constant for the first order.[6]

The wave-lengths of the various lines in the spectrum of sulphur and the various sulphides studied are given in Table I.

TABLE I. *Wave-lengths of the x-ray emission lines of sulphur in X-units.*

Line	S	FeS	CoS	NiS	Cu_2S	ZnS
α_2	5363.50	5364.35	5364.16	5364.05	5363.97	5364.27
α_1	5360.39	5361.28	5361.34	5361.05	5360.94	5361.29
α'	5342.1	5343.0	5342.7	5342.1	5342.4	5342.7
α_3	5330.21	5330.75	5330.77	5330.49	5330.39	5330.61
α_3'	5327.5	5328.2	5328.4	5328.1	5328.2	5328.1
α_4	5323.27	5324.12	5324.04	5323.52	5323.45	5323.89
α_5	5284.5	5285.2	5286.0	5284.2	5285.1	5285.4
β_4	—	5065.24	5065.26	5066.02	—	—
β_5	—	—	—	—	—	5030.4
β_1	5020.72	—	5020.89	—	5021.84	5023.77
$\beta_{1,2}$	—	5017.3	—	5018.4	—	5016.95
β_2	5013.35	—	5012.62	—	5013.39	—

The α_1 and α_2-lines are probably correct within ± 0.1X, while the others may be in error by ± 0.1 up to ± 0.4X according to their breadth and intensity. The α_5-lines were particularly difficult to measure.

Other faint lines which were occasionally observed and seem to be due to sulphur or sulphides are as follows: 5108, 5043, 4953, 4936, and 4900. These values may be in error by ± 2X. Of these, the 5108 and 4900 lines were most frequently observed.

The α-group is seen to change very little from compound to compound. This is surprising in view of the fact that the K absorption edges shift by 2 to 4X-units.[8] Evidently these shifts are closely paralleled by the shifts in the L levels.

On the other hand, the β-lines show widely different appearances in some cases. This is clearly illustrated in Fig. 2 which summarizes the results for these lines. The spectra of CoS and NiS have not been previously observed. The CoS was prepared by precipitation from cobalt nitrate by ammonium sulphide. The NiS was the mineral, millerite. The spectrum of ZnS is entirely different from the single broad line heretofore described in the literature. The spectrum here obtained was the same when the copper target was replaced by iron. The spectrum of pure sulphur showed only a slight dependence on the target material. This result could not have been obtained by the usual procedure of electron impact directly on the powdered sulphur.

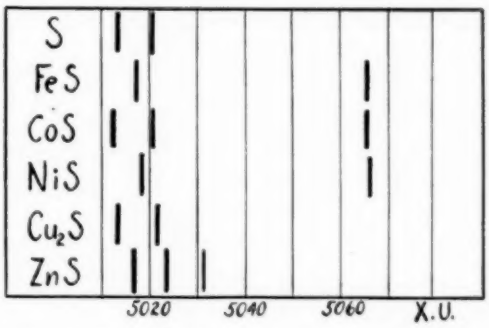

FIG. 2. The $K\beta$-lines of sulphur and sulphides.

However, extreme care must be exercised if the electrode influence is to be entirely eliminated, particularly if the substance is easily fused or

[5] Eriksson, Zeits. f. Physik **48**, 360 (1928).

[6] Siegbahn, *Spektroskopie der Roentgenstrahlen*, 2nd edition, p. 44.

[7] Lindh, *Roentgenspektroskopie*, p. 63.

[8] Lindh, *Roentgenspektroskopie*, p. 291.

volatilized. This is due to the almost unavoidable contamination of the target which usually gives a scarcely perceptible target sulphide spectrum superposed on that of the compound. This can be reduced to negligible proportions by applying proper care. The target must be kept smooth and clean.

It is surprising that the frequently observed β_3-line could only be seen on two of the plates, namely, two heavily exposed ZnS plates, and that on these it was scarcely visible. On the other hand, two of Deodhar's recently discovered "weak" lines, namely β_4 and β_5, were quite strong in some cases. The β_4-line is a prominent line in the CoS and FeS spectra, while β_5 appeared in the ZnS spectrum.

The reasons for the observed differences in the β-lines of various sulphides are not clear. One may think of a readjustment of the outer energy levels of the combining elements to some common mean value. It would be of interest to study this question by means of the spectra of the metallic elements in the sulphides. A start has already been made on this problem, and it has been found that the $K\beta_1$-line of iron is strongly shifted in the sulphide to 1758.46X, while its wave-length in the spectrum of pure iron is 1753.01X. In energy units, this shift is approximately equal to the difference between the S $K\beta_4$ and S $K\beta_{1X}$-lines and is in the same direction. A further study of these effects is in progress.

The method of examination here described makes it a relatively simple matter to compare the spectra of various crystal modifications of the same compound. Insofar as this has been done, (ZnS as zincblende and wurtzite) there seems to be no appreciable effect of crystal modification on the x-ray spectrum. This study is being continued.

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Projective Relativity and the Einstein-Mayer Unified Field Theory

BANESH HOFFMANN, *Department of Mathematics, University of Rochester, N. Y.*

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The relationship between the Einstein-Mayer unified field theory and the projective relativity theory is developed and it is shown that the field equations (47) of the former theory may be interpreted as conditions that the connection employed be reducible to a symmetric form by means of a suitable non-holonomic factor change. Grounds are found for questioning an assumption made by Schouten and Van Danzig.

§1. INTRODUCTION

IN 1921 Kaluza put forward the idea that the addition of a specialized fifth dimension to the space-time of the general theory of relativity would provide a mechanism for the construction of a unified theory of gravitation and electromagnetism and this was shown to be rigorously the case by Klein. The fact that no physical significance could be given to the fifth dimension was a considerable drawback to the Kaluza-Klein theory and this objection was removed in the projective relativity theory[1] the formalism of which closely parallels that of the five-dimensional theory. In 1931 Einstein and Mayer[2] introduced a new unified field theory that was also based upon the Kaluza model but, like the projective theory, was four-dimensional; this theory has been further considered and modified by Schouten and Van Danzig,[3] and also by Veblen in a forthcoming book. It is known that the various theories are closely related and in the present paper it is proposed to discuss certain formal relations between them.[4] We shall be concerned here solely with the first of the Einstein-Mayer papers cited; the second carries the theory beyond the stage it attained in the first of these papers but the physical significance of this advance has not yet been investigated.

§2. ON THE ALGEBRAIC FORMALISM OF THE EINSTEIN-MAYER THEORY

We begin by considering §1 of the first Einstein-Mayer paper in terms of a slightly modified formalism which depends upon the replacing of the singular transformation there used by a non-singular one. We shall refer to the Einstein-Mayer theory as E–M and to equations occurring in their first paper upon it as E–M(2), etc. The projective theory will likewise be referred to as P.R. and equations in *Projective Relativity* as P.R.(2), etc.; we shall deal with P.R. only for the case $\Phi=1$. Greek suffixes will always take on the values 0, 1, 2, 3, 4 and Latin suffixes the values 1, 2, 3, 4. We shall have to deal with two types of reference system; for the one we shall always reserve the letters $\alpha, \beta, \gamma, \cdots; a, b, c, \cdots$, and for the other the letters $\lambda, \mu, \nu, \cdots; l, m, n, \cdots$; to distinguish the null suffix in the λ-system from that in the α-system we shall denote the former by θ.

To avoid complication we prefer to deal with the projective space in terms of its five-dimensional representation. Let x^λ be the coordinates of such a representation of which x^l are the ordinary coordinates of space-time; furthermore let all geometric objects be such that their components are independent of x^θ, and let us decide to keep the factor x^θ unchanged in the λ-system.

[1] See O. Veblen, "A Generalisation of the Quadratic Differential Form," Q. J. Math. (Oxford) **I**, 60–76 (1932), and O. Veblen and B. Hoffmann, "Projective Relativity," Phys. Rev. **36**, 810–822 (1930) where references are given.

[2] Einstein and Mayer, Sitz. der Preuss. Akad. (Berlin) **XXV**, 541–557 (1931), and also **XII**, 130–137 (1932).

[3] Schouten and Van Danzig, Proc. Roy. Acad. (Amsterdam) **XXXIV**, 1398–1407 (1931), and also Zeits. f. Physik **78**, 639–667 (1932).

[4] Most of the work of the present paper was performed before the appearance of the second of the Schouten-Van Danzig papers and some degree of overlapping will be apparent in the present paper.

Let $g_{\lambda\mu}$ be such that

$$g_{\lambda\mu}=\delta_{\lambda\mu}; \tag{1}$$

by means of the "mixed" tensor $\gamma_\alpha{}^\lambda$ we define alternative components for all geometric objects, and thus for the metric, $g_{\lambda\mu}$, we have the α-components, $g_{\alpha\beta}$, given by

$$g_{\alpha\beta}=\gamma_\alpha{}^\lambda\gamma_\beta{}^\mu g_{\lambda\mu}=\gamma_\alpha{}^l\gamma_\beta{}^m g_{lm}+\gamma_\alpha{}^\theta\gamma_\beta{}^\theta. \tag{2}$$

If we set

$$\gamma_\alpha{}^\theta=A_\alpha \tag{3}$$

the restriction that x^θ be invariant means that A_α behaves like an α-vector and Eq. (2) becomes

$$g_{\alpha\beta}=\gamma_\alpha{}^l\gamma_\beta{}^m g_{lm}+A_\alpha A_\beta \tag{4}$$

which is identical with E–M (13b).

Since $g_{\lambda\theta}=\delta_{\lambda\theta}$ we have from $g_{\lambda\theta}g^{\lambda\mu}=\delta_\theta{}^\mu$ that

$$g^{\theta\lambda}=\delta^{\theta\lambda}; \tag{5}$$

then, defining $\gamma_l{}^\alpha$ and A^α as the result of raising and lowering indices of $\gamma_\alpha{}^l$ and A_α with appropriate g's as in E–M, we have

$$\gamma_\alpha{}^l A^\alpha=g^{\alpha\beta}\gamma_\alpha{}^l A_\beta=g^{l\theta}=0 \tag{6}$$

which is E–M (10). We have also, at once, that

$$g_{\alpha\beta}A^\alpha A^\beta=g_{\theta\theta}=1 \tag{7}$$

which is E–M (11).

Let b be a vector; then $b_\lambda=\gamma_\lambda{}^\alpha b_\alpha$ or

$$b_l=\gamma_l{}^\alpha b_\alpha \tag{8}$$

and

$$b_\theta=A^\alpha b_\alpha; \tag{9}$$

Eq. (8) is E–M (14), (the second E–M (14)!). Again, the inverse transformation is

$$b^\alpha=\gamma_\lambda{}^\alpha b^\lambda=\gamma_l{}^\alpha b^l+A^\alpha b^\theta$$

and using (9) and (5) this is

$$\begin{aligned} b^\alpha&=\gamma_l{}^\alpha b^l+A^\alpha A^\beta b_\beta \\ &=\gamma_l{}^\alpha b^l+\rho A^\alpha, \quad (\rho=A_\beta b^\beta) \end{aligned} \tag{10}$$

as in E–M.

§3. Covariant Derivation

Denoting covariant derivation with regard to a connection Γ by means of a solidus let us require that

$$g_{\lambda\mu/\nu}\equiv 0 \tag{11}$$

and also that

$$g_{\alpha\beta/\nu}\equiv 0; \tag{12}$$

it is a well-known result that (11) gives

$$\Gamma_{\mu\nu}{}^\lambda=\left\{\begin{matrix}\lambda\\ \mu\nu\end{matrix}\right\}+g^{\lambda\sigma}(S_{\mu\nu\sigma}+S_{\nu\mu\sigma}+S_{\sigma\mu\nu}) \tag{13}$$

where $\left\{\begin{matrix}\lambda\\ \mu\nu\end{matrix}\right\}$ are the Christoffel symbols formed from the $g_{\lambda\mu}$, and $S_{\lambda\mu\nu}$ is an arbitrary tensor antisymmetric in the second and third indices. Since $g_{\lambda\theta}=\delta_{\lambda\theta}$ and the $g_{\lambda\mu}$ are independent of x^θ it is at once found that

$$\left\{\begin{matrix}\lambda\\ \mu\nu\end{matrix}\right\}=\left\{\begin{matrix}l\\ mn\end{matrix}\right\}\delta_l{}^\lambda\delta_\mu{}^m\delta_\nu{}^n, \tag{14}$$

where $\left\{\begin{matrix}l\\ mn\end{matrix}\right\}$ are the Christoffel symbols formed from the g_{lm}.

Instead of taking the general Γ given by (13) we shall impose the restriction that

$$\left.\begin{aligned} &S_{\lambda\mu\nu}=\delta_{\theta\lambda}\delta_\mu{}^m\delta_\nu{}^n F_{mn}, \\ &\text{where, necessarily,} \\ &F_{mn}=-F_{nm} \\ &\text{and is an affine tensor;} \end{aligned}\right\} \tag{15}$$

this is an invariant restriction since θ is a scalar suffix.

As a result of (15) we now have

$$\left.\begin{aligned} &\Gamma_{mn}{}^l=\left\{\begin{matrix}l\\ mn\end{matrix}\right\},\ \Gamma_{m\theta}{}^l=\Gamma_{\theta m}{}^l=F_m{}^l,\ \Gamma_{lm}{}^\theta=F_{lm}, \\ &\qquad\qquad\qquad\qquad\qquad\text{the rest being zero.} \end{aligned}\right\} \tag{16}$$

The conditions (12) will not suffice to give the law of transformation from $\Gamma_{\mu\nu}{}^\lambda$ to $\Gamma_{\beta\nu}{}^\alpha$; we impose the following condition which is consistent with the condition that (12) be a result of (11); let b_λ be any vector and $b_{\lambda/\mu}$ its covariant derivative, and let $b_{\alpha/\mu}$ be the covariant derivative of the corresponding b_α; we require that

$$b_{\alpha/\mu}=\gamma_\alpha{}^\lambda b_{\lambda/\mu};$$

the law of transformation from $\Gamma_{\mu\nu}{}^\lambda$ to $\Gamma_{\beta\nu}{}^\alpha$ given by this condition is then

$$\gamma_\gamma{}^\nu\Gamma_{\alpha\mu}{}^\gamma=\gamma_\alpha{}^\lambda\Gamma_{\lambda\mu}{}^\nu+\frac{\partial}{\partial x^\mu}\gamma_\alpha{}^\nu. \tag{17}$$

By using (3) and (16) this becomes

$$\left.\begin{aligned}\gamma_\gamma{}^n\Gamma_{\alpha m}{}^\gamma &= \gamma_\alpha{}^l\begin{Bmatrix} n \\ lm\end{Bmatrix} + A_\alpha F_m{}^{\cdot n} + \frac{\partial}{\partial x^m}\gamma_\alpha{}^n,\\ A_\gamma\Gamma_{\alpha m}{}^\gamma &= \gamma_\alpha{}^l F_{lm} + \frac{\partial}{\partial x^m}A_\alpha,\end{aligned}\right\} \quad (18a)$$

and

$$\gamma_\gamma{}^n\Gamma_{\alpha\beta}{}^\gamma = \gamma_\alpha{}^l F_l{}^{\cdot n}, \quad A_\gamma\Gamma_{\alpha\beta}{}^\gamma = 0. \quad (18b)$$

The Eqs. (18b) serve to define, in terms of F and γ, the quantities $\Gamma_{\alpha\beta}{}^\gamma$ which, like the $\Gamma_{\mu\beta}{}^\lambda$, do not enter the formalism of E–M explicitly; thus the present $\Gamma_{\alpha\beta}{}^\gamma$ and $\Gamma_{\mu\beta}{}^\lambda$ do not involve any quantities that are not contained in the other components of Γ.

By using a semi-colon to denote E–M covariant derivation and identifying the present $\Gamma_{\beta m}{}^\alpha$ with that of E–M, (18a) become

$$\gamma_\alpha{}^n{}_{;\,m} = A_\alpha F^n{}_{\cdot m}, \quad A_{\alpha;\,m} = -\gamma_\alpha{}^l F_{lm}, \quad (19)$$

which are E–M (2) and (27), upon which the whole of the subsequent work in E–M is based.

The Eqs. (19), together with (18b), are merely an expression of the relation

$$\gamma_\alpha{}^\lambda{}_{/\mu} \equiv 0 \quad (20)$$

which is thus $g_\alpha{}^\beta{}_{/\mu} \equiv 0$ in a different mixed reference system.

§4. Trajectories

The E–M trajectories may be defined as the curves generated by the parallel displacement of the vector dx^λ/dt along the corresponding direction dx^l/dt, *the displacement being according to the connection* Γ; for, such curves are given by

$$\frac{dx^m}{dt}\left(\frac{dx^\lambda}{dt}\right)_{/m} = 0, \quad (21)$$

i.e., by

$$d^2x^\lambda/dt^2 + \Gamma_{\nu m}{}^\lambda(dx^m/dt)(dx^\nu/dt) = 0$$

or, using (16), by

$$\frac{d^2x^l}{dt^2} + \begin{Bmatrix} l \\ mn\end{Bmatrix}\frac{dx^m}{dt}\frac{dx^n}{dt} - F^l{}_{\cdot m}\frac{dx^m}{dt}\frac{dx^\theta}{dt} = 0, \quad \frac{d^2x^\theta}{dt^2} = 0.$$

Thus from the second

$$dx^\theta/dt = \rho, \quad (\rho = \text{const.})$$

and the remaining equations become

$$\frac{d^2x^l}{dt^2} + \begin{Bmatrix} l \\ mn\end{Bmatrix}\frac{dx^m}{dt}\frac{dx^n}{dt} = \rho F^l{}_{\cdot m}\frac{dx^m}{dt},$$

which are E–M (28).

The above treatment is essentially the expression of the E–M treatment in terms of the λ-system only and is formally the same as that of Schouten and Van Danzig.

§5. The Field Equations E–M (47)

The field Eqs. E–M (47), namely

$$F_{lm,\ n} + F_{mn,\ l} + F_{nl,\ m} = 0, \qquad \text{E–M (47)}$$

have no counterpart, *as field equations*, in the Kaluza-Klein theory, in P.R. or in the theory of Schouten and Van Danzig, though in the last they enter implicitly as a formal assumption; in all these theories the above field equations are identically satisfied. They imply that there exists a four-vector, say B_l, arbitrary to within an additive gradient and such that

$$F_{lm} = \partial B_l/\partial x^m - \partial B_m/\partial x^l. \quad (22)$$

Let us specialize the γ's by imposing the requirements that

$$A_0 = 1, \quad \gamma_\alpha{}^l = \delta_\alpha{}^l, \quad (23)$$

and let us consider the quantities $g_{\alpha\beta}$ and $\Gamma_{\beta\gamma}{}^\alpha \equiv \Gamma_{\beta\nu}{}^\alpha\gamma_\gamma{}^\nu$ when this specialization has been made; the restrictions (23) imply that the α- and λ-systems are now related by a non-holonomic change of factor, the space-time coordinates remaining unchanged.

The antisymmetric part of a connection does not behave as a tensor under changes of reference system of the present type and therefore although $\Gamma_{\mu\nu}{}^\lambda$ be unsymmetric it will not necessarily follow that $\Gamma_{\beta\gamma}{}^\alpha$ is unsymmetric also; the law of transformation of Γ is

$$\gamma_\alpha{}^\lambda\Gamma_{\beta\gamma}{}^\alpha = \Gamma_{\mu\nu}{}^\lambda\gamma_\beta{}^\mu\gamma_\gamma{}^\nu + \gamma_\gamma{}^\mu(\partial\gamma_\beta{}^\lambda/\partial x^\mu) \quad (24)$$

and the condition that $\Gamma_{\beta\gamma}{}^\alpha$ be symmetric is therefore that

$$(\Gamma_{\mu\nu}{}^\lambda - \Gamma_{\nu\mu}{}^\lambda)\gamma_\beta{}^\mu\gamma_\gamma{}^\nu + \gamma_\gamma{}^\mu\frac{\partial}{\partial x^\mu}\gamma_\beta{}^\lambda - \gamma_\beta{}^\mu\frac{\partial}{\partial x^\mu}\gamma_\gamma{}^\lambda = 0, \quad (25)$$

which, by (23) and (16), gives merely

$$2F_{mn}\delta_\beta{}^m\delta_\gamma{}^n+\delta_\gamma{}^m(\partial A_\beta/\partial x^m)-\delta_\beta{}^m(\partial A_\gamma/\partial x^m)=0$$

or

$$2F_{mn}=\partial(A_a\delta_m{}^a)/\partial x^n-\partial(A_a\delta_n{}^a)/\partial x^m. \quad (26)$$

This can only be satisfied if E–M (47) is satisfied; thus the equation E–M (47) may be interpreted as the necessary and sufficient condition that it be possible so to choose the A_α, the $\gamma_a{}^l$ being restricted according to (23) and the quantities $\Gamma_{\beta\vartheta}{}^\alpha$, $\Gamma_{\mu\theta}{}^\lambda$ being given by (18b), (16), that the connection $\Gamma_{\beta\gamma}{}^\alpha$ be symmetric; and in this case F_{mn} is given by (26).

Moreover the $g_{\alpha\beta}$, by (4), are now given by

$$g_{ab}=\delta_a{}^m\delta_b{}^n g_{mn}+A_aA_b,\ g_{a0}=A_a,\ g_{00}=A_0=1, \quad (27)$$

and, since the physical significance of the g_{mn} is that of being the gravitational potential, and of A_a that of being, by (26), the electromagnetic potential, the present $g_{\alpha\beta}$ has both the form and the physical significance of the $\gamma_{\alpha\beta}$ of P.R.[5] except for a difference in sign between the definitions of the φ_{mn} of P.R. and the F_{mn} of E–M.[6] Now the introduction of the F_{mn} in the E–M theory does not fix the sign to be attached to it and the equation E–M II could as well have been written

$$\gamma_{k;\,q}=-A^lF_{kq}\ ,$$

since the field equations contain the F_{mn} either in the form of a homogeneous quadratic function, as in E–M (46a), or else, as in E–M (46b) and E–M (47), as

$$f=0,$$

where f is a homogeneous linear function of the F_{mn}; and therefore so far as the field equations are concerned the sign of F_{mn} is immaterial.

Thus, if we consider the F of E–M to be replaced by its negative, and if we satisfy E–M (47) identically through the requirement that $\Gamma_{\beta\gamma}{}^\alpha$ be symmetric when the γ's are given by (23), we have a one-to-one correspondence between the basic formulas and field equations of P.R. and E–M.

§6. The Field Equations E–M (47), (Continued)

In the preceding sections we exhibited a relationship between the E–M theory and P.R. on the basis of a special choice of the quantities $\Gamma_{\mu\theta}{}^\lambda$ that are not completely determined by the E–M theory, and this relationship gave to the vector A the physical significance of being the electromagnetic potential, the tensor F being the curl of A; in the present section we wish to discuss the relationship between F and A more fully than was done in the previous section, where we were concerned with deriving the relationship between P.R. and E–M.

The equations E–M (47) imply that there is a four-vector, which we shall write as $B_a\delta_m{}^a$, such that

$$F_{mn}=\partial(B_a\delta_m{}^a)/\partial x^n-\partial(B_a\delta_n{}^a)/\partial x^m; \quad (22a)$$

it is evident that if we keep the special values that were assumed for the $\Gamma_{\mu\theta}{}^\lambda$ in the previous sections we can find a set of γ's, corresponding to a non-holonomic factor change, such that the new metric will contain the B as the electromagnetic potential in the manner of P.R.; the factor change in question is merely

$$\gamma_\theta{}^m=\delta_\theta{}^m,\quad \gamma_a{}^\theta=B_a,\quad (B_0=1), \quad (23a)$$

i.e., (23) with B written in the place of A; from the work of §5, if we continue to write B for A, we have at once that the new $\Gamma_{\beta\gamma}{}^\alpha$ is symmetric. Thus we have proved a theorem closely related to that of §5; in §5 we started with A as given and satisfied E–M (47) by its means through the condition that $\Gamma_{\beta\gamma}{}^\alpha$ be symmetric. In the present section we started with any solution of E–M (47); this solution defines a vector B (to within a gradient) and it is shown that this vector B can always be made to play the part played by the vector A in §5, the $\Gamma_{\beta\gamma}{}^\alpha$ at the same time being made symmetric automatically.

The above was on the assumption that the $\Gamma_{\mu\theta}{}^\lambda$ were chosen in a special manner not forced upon us by the formalism of E–M; let us now drop this restriction upon Γ. The E–M theory is based essentially upon the Eqs. (19); from the first of these it is seen that we must necessarily have

$$\Gamma_{mn}{}^l=\left\{\begin{matrix} l \\ mn \end{matrix}\right\};\quad \Gamma_{\theta m}{}^l=F_m{}^l;\quad \text{and}\quad \Gamma_{\theta m}{}^\theta=0$$

and from the second of them we must add to this list

$$\Gamma_{lm}{}^\theta=F_{lm}.$$

[5] Compare P.R. (3.1).

[6] Compare P.R. p. 815 with the Eq. (26) of the present paper.

Thus the values we have used for the components $\Gamma_{\mu n}{}^{\lambda}$ were forced upon us; it does not follow, however, that since the $\Gamma_{\mu\theta}{}^{\lambda}$ are not contained in (19) they may be taken as arbitrary; for their values depend on the values of the components of the tensor $S_{\lambda\mu\nu}$ of (13) and this S must give the $\Gamma_{\mu n}{}^{\lambda}$ correctly. It is not difficult to find to what extent the quantities $\Gamma_{\mu\theta}{}^{\lambda}$ are arbitrary, and for this purpose it is unnecessary to consider explicitly the alternative forms of S that may be used whilst still keeping the old values of $\Gamma_{\mu n}{}^{\lambda}$; for we need merely express the condition

$$g_{\lambda\mu/\nu}\equiv 0,$$

which must be satisfied by $\Gamma_{\mu\nu}{}^{\lambda}$, of which $\Gamma_{\mu n}{}^{\lambda}$ are already determined. The only equations in which $\Gamma_{\mu\theta}{}^{\lambda}$ appear are

$$g_{\lambda\mu/\theta}\equiv 0,$$

which, since g is independent of x^{θ}, gives

$$g_{\sigma\mu}\Gamma_{\lambda\theta}{}^{\sigma}+g_{\sigma\lambda}\Gamma_{\mu\theta}{}^{\sigma}=0;$$

and, remembering that $g_{\lambda\theta}=\delta_{\lambda\theta}$, this at once gives

$$\Gamma_{m\theta}{}^{\theta}=\Gamma_{\theta\theta}{}^{\theta}=0, \quad g_{ms}\Gamma_{l\theta}{}^{s}+g_{ls}\Gamma_{m\theta}{}^{s}=0, \quad (28)$$

which limits the arbitrariness of $\Gamma_{\mu\theta}{}^{\lambda}$.

We may now answer the question, what restrictions do the field equations E–M (47) place upon Γ; evidently the most general Γ that is possible if E–M (47) are satisfied is given by

$$\Gamma_{mn}{}^{l}=\left\{\begin{matrix} l \\ mn \end{matrix}\right\}, \ \Gamma_{\theta m}{}^{l}=F_{m}{}^{\cdot l}, \ \Gamma_{lm}{}^{\theta}=F_{lm}, \ \Gamma_{m\theta}{}^{l}=g^{ls}K_{ms},$$

where

$$F_{lm}=(\partial B_l/\partial x^m-\partial B_m/\partial x^l) \text{ and } K_{ms}=-K_{sm},$$

and all the components of $\Gamma_{\mu\nu}{}^{\lambda}$ not included in the above are zero.

The Schouten and Van Danzig interpretation of E–M implies that the antisymmetric tensor K_{lm} is a multiple of the curl of the vector B, and the above would seem to show that such an assumption goes beyond the actual content of the E–M theory.

Neutrons in the Nucleus. I

ALFRED LANDÉ, *Ohio State University, Mendenhall Laboratory of Physics*

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It is supposed that the nucleus consists of α-particles, neutrons and zero or one proton, instead of the former structure scheme, α-particles, electrons and 0, 1, 2, 3 protons. The calculated mass defects Δm of the isotopes of a single element show an exact linear increase of Δm with the mass number (instead of the fluctuating function in the former structure scheme). The Δm-difference of the isotopes of each element is rather constant throughout the periodic system for even elements. The absolute values of the mass defects give a potential energy curve decreasing uniformly with increasing atomic number (instead of showing a minimum at the element No. 50 in the former structure scheme). In the region of the radioactive substances the energy curve seems to turn up again. All of this helps the model that the isotopes of an element differ only by the number of neutrons incorporated by them, the binding energy per neutron being rather constant throughout the periodic system and about 0.009 in mass units for even elements. In several cases the isotopes give a picture of the construction of a complete outer shell of 8 or 12 neutrons and indications that also in other cases there is a shell structure of the neutron arrangement, but none of the α-particles. The empirical rule that odd elements have no isotopes with even mass numbers can be explained, together with its exceptions, by help of the neutron structure scheme.

FOLLOWING Heisenberg,[1] who has explained several facts about the existence and stability of isotopes by help of neutrons and protons, we assume that the building stones of the nucleus consist of α-particles, zero or one loose proton, and neutrons. It may be of interest to support this model from some other points of view throughout the periodical table, stressing more than does Heisenberg the rôle of the α-particles in the whole nuclear structure.

I. Isotopes of a Single Element

There are only a few elements with several isotopes whose atomic weights have been measured to three decimals, so that one can calculate their mass defects with sufficient accuracy. These are Kr 36 (6 isotopes), Sn 50 (11 isotopes), Xe 54 (9 isotopes), Hg 80 (9 isotopes). Now the former theory interprets the structure of the Xe-isotopes $Z=54$ in the following way:

$$Xe^{124}=31\alpha+8\text{ el},$$

$$Xe^{125}, \text{ missing},$$

$$Xe^{126}=31\alpha+10\text{ el}+2\text{ pr},$$

$$Xe^{127}, \text{ missing},$$

$$Xe^{128}=32\alpha+10\text{ el},$$

$$Xe^{129}=32\alpha+11\text{ el}+1\text{ pr},$$

$$\text{etc.}$$

assuming four different numbers of α-particles from 31 to 34. This scheme gives the following values for the mass defects of the nine isotopes (compare the mass-spectrum of Xe in Table II): 0.133, —, 0.150, —, 0.137, ?, 0.154, 0.162, 0.141, —, 0.158, —, 0.154, which are seen to fluctuate with increasing mass of the isotope (compare Gamow's Table II of reduced weights with He = 4.000).

Now since Aston's weights[2] of the Xe-isotopes increase from 123.867 to 135.855 in almost exactly equal steps (passing over the missing isotopes) it is rather unsatisfactory to account for this linear rise by a fluctuating function. One has rather to explain it by a linear sequence of equal binding processes. In the scheme of neutrons (ν) the Xe-isotopes are to be described by

$$Xe^{124}=27\alpha+16\nu \quad \text{to} \quad Xe^{136}=27\alpha+28\nu.$$

Here the mass defect of Xe^{124} becomes $27\times 4.000+16\times 1.0075+16\times 0.0005-m_{\text{observed}}=0.261$, representing the energy required to split up the nucleus into 27 α-particles and 16

[1] W. Heisenberg, Zeits. f. Physik **78**, 150 (1932).

[2] G. Gamow, *Atomic Nuclei and Radioactivity*, Oxford, 1931.

neutrons and break up each neutron into its components. The last part could be separated if we knew the exact atomic weight of the neutron. If one calculates in the same way the mass defects of all Xe-isotopes, one gets the results: 0.261, —, 0.279, —, 0.297, ?, 0.315, 0.324, 0.333, —, 0.351, —, 0.369, indicating a *linear increase* of the defect by equal steps of 0.009 each, parallel to the observed linear steps of the atomic weights. This result is based on the assumption that all of the Xe-isotopes consist of 27 α-particles and 16 to 28 neutrons, the energy required to split off each neutron from the nucleus of Xe and to break it up into a proton and an electron being exactly constant, equal to 0.009 in mass units.

II. Isotopes of Various Elements

If one carries out the same calculations for the isotopes of other elements insofar as their atomic weights are sufficiently determined, one obtains in all cases the same exact linearity of the mass defects, parallel to the fact that the observed atomic weights of the isotopes form a linear set. We have then merely to report the constant intervals between subsequent mass defects for various elements, among them 0.009 for Xe. These are given in Table I for those

Table I. *Mass defect differences.*

6 C	0.008	54 Xe	0.009
10 Ne	0.006	80 Hg	0.008
18 Ar	0.009	3 Li	0.009
36 Kr	0.008	5 B	0.013
42 Mo	0.008	17 Cl	0.011
50 Sn	0.009	35 Br	0.010

elements with more than one isotope, whose atomic weights are known up to 3 decimals.

We interpret then the values of Table I as the energy in mass units to split off one neutron and to break it up. The atoms of even charge number display in general many more isotopes than the odd elements. For even elements the binding energy per neutron seems rather constant throughout the periodic system except for Ne. The binding energy per neutron for odd elements is more variable and on the average a little larger than for even elements. This may be due to the one extra proton which increases the attraction of the neutrons and disturbs the symmetry of the neutron arrangement.

III. Nuclear Stability Throughout the Periodic Table

If one plots the mass defects according to the old theory (α-particles, loose electrons and 0, 1, 2, 3 loose protons) one obtains for the potential energy of the nuclei a distribution having a minimum in the range of element number 50 (compare Gamow's Fig. 16). This minimum is a serious difficulty, because it means that the elements above 50 should be unstable, while in fact they are unstable above 80. If however we plot the mass defects according to the new scheme (α-particles, neutrons and 0 or 1 proton), then we obtain the mass defects given in Fig. 1. Each mass defect dot is marked with the number of neutrons contained in the isotope. The figure shows a *general decrease of the potential energy* with increasing atomic number. Among the radioactive substances the weights of Ra, Th and U are determined to only 2 decimals, in which the last one is not certain. So we have drawn dashes instead of dots in the region of their probable mass defects. Among the lighter elements the measured weights are rather incomplete, and sometimes only one of several isotopes could be used in our figure for that reason. The potential energy seems to have a minimum just in the region of the radioactive substances, where stable elements cease to exist. That our Δm increases uniformly while the curve of Gamow's book bends up after 50 is due to the fact that in the old scheme the number of α-particles is larger than in the neutron theory. For instance Hg 80 with $m = 196$ to 204 has in the old scheme 49 to 51 α-particles, in the neutron scheme only 40.

IV. Existence of Odd Charged Nuclei

The rules of Harkins concerning the relative abundance of the elements and their isotopes throughout the periodic table read in our scheme: Elements with a loose proton (odd charge number) are much rarer than elements without a loose proton (even charge number). Furthermore if we consider first only even elements we find that isotopes with an even number of neutrons are more frequent than those with an odd number of neutrons. Missing isotopes in most cases belong to odd neutron arrangements. *This fact cannot be*

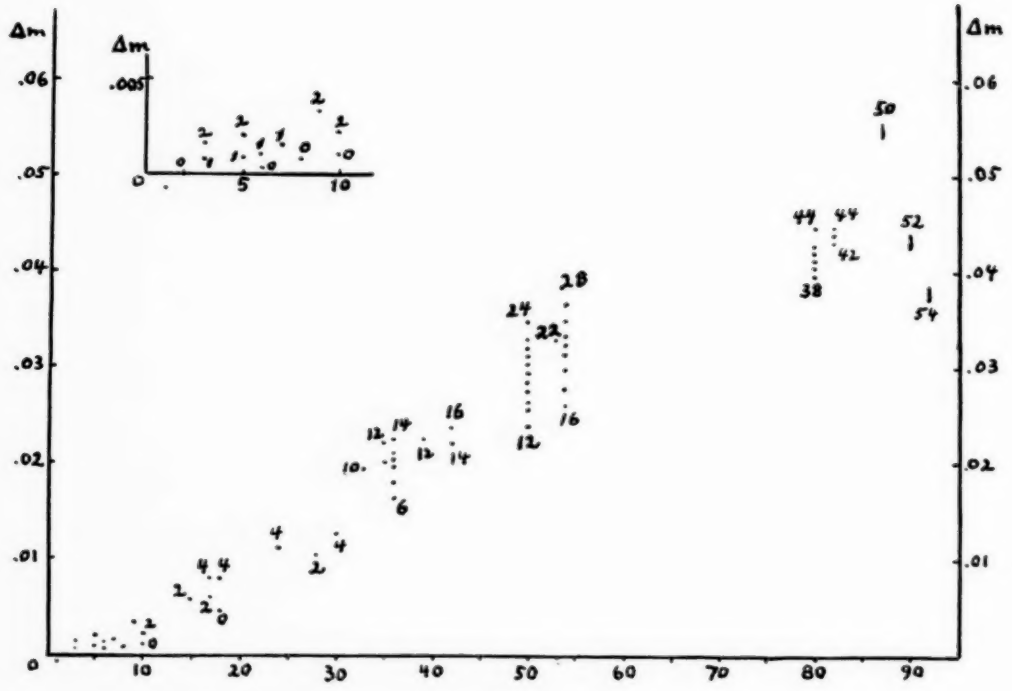

FIG. 1.

explained by energy balances, since we learned in Part I that the successive incorporation of one neutron after the other produces a linear increase of the mass defect without any break, at least for the neutrons added last. We have then to take for granted the preference of even arrangements of neutrons without an explanation by energy balances.

As to the elements of odd charge number one may wonder why they exist at all, both with even and odd numbers of neutrons. For if processes of *β-emission* connected with a transformation of one of the neutrons into a proton are taken into account, then the original loose proton and the new proton should associate with two neutrons to form an α-particle, and the odd element should pass over into an even one. However, though the final product has one α-particle more, it has three neutrons less. Now we learn from Table I that the energy gain 0.032 of building up an α-particle is about the energy loss of separating three neutrons and one β-particle from the nucleus; so these two effects may approximately balance each other, and we expect that minor secondary causes shall give the *decision* whether an element of odd charge number is or is not stable.

Now experience shows as a rule that odd elements have isotopes with odd mass numbers only, or expressed in our scheme: *Odd elements have no isotopes with an odd number of neutrons.*

We can explain this rule in the following way. The above-mentioned β-emission transforms an odd arrangement of neutrons into an even one. If there is only a small preference of even neutron arrangements before odd ones, this may give the decision mentioned above that the β-emission in this case always will happen, hence odd arrangements of neutrons in odd elements will be unstable. In the reverse case, if an even number of neutrons has only a small tendency to remain even instead of turning odd, this will give the decision that the β-emission is barred, and the isotope is stable.

This consideration does not hold if the odd number of neutrons is just *unity*. For then a β-emission would leave no neutron to form a new α-particle. In fact, there are four exceptions to the rule, namely, the existence of the stable isotopes, H^2, Li^6, B^{10}, N^{14}. But these are just four

cases in which our structure scheme gives *one* neutron only, namely:

$$H^2 \ldots\ldots\ldots 0\alpha + 1\,\text{pr} + 1\nu$$

$$Li^6 \ldots\ldots\ldots 1\alpha + 1\,\text{pr} + 1\nu$$

$$B^{10} \ldots\ldots\ldots 2\alpha + 1\,\text{pr} + 1\nu$$

$$N^{14} \ldots\ldots\ldots 3\alpha + 1\,\text{pr} + 1\nu$$

Thus from the point of view of the neutron scheme the four exceptions prove the rule. The same holds for the exceptions among the radioactive elements giving β-rays.

V. Neutron Shells

It is very tempting but precarious to conclude from the table of the isotopes known up to now details of the arrangement of the neutrons in the nucleus. The existence of closed shells of neutrons is suggested by the fact, so striking at the first view of an isotopic table, of similar isotope sequences repeated in different elements. Consider for instance the following cases of mass-spectra given in Table II. Missing isotopes are

Table II. *Mass-spectra.*

Ge 32	Se 34	Kr 36	Mo 42	Ru 44	Hg 80	Pb 82	Po 84	Sn 50	Xe 54
·	–	–	–	–	–	–	–	–	–
–	·	·	·	·	(–)	·	·	·	·
–	–	–	–	–	–	–	–	–	–
–	·	·	–	–	–	–	–	–	·
–	–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	·	·	·	–
–	–	–	–	–	–	·	–	–	–
–	·	·	·	·	(–)	–	–	–	–
–	–	–	–	–	–	–	–	–	–
								–	·
								–	–
								·	·
								–	–
6ν	6ν	6ν	8ν	8ν	36ν	42ν	42ν	12ν	16ν

indicated by dots. The second line means the charge number of the element, the last line of the table indicates the number of neutrons contained in the isotopes of lowest mass. We interpret this number as the total number in complete or incomplete inner neutron shells, to which neutrons are then attached step by step until an outer shell is completed. The examples of Table II we interpret as the incorporation of an outer shell of 8 or of 12 neutrons. As to the dots we observe that usually odd arrangements of neutrons are missing. With Se, Kr, Mo, Ru and also Sn and Xe, the isotopes with *one* neutron in the outer shell and the isotope with *one* neutron lacking in the outer shell are not observed. Whether this is essential or merely due to small intensity may be judged from the case of Hg. Here Aston's first experiments missed these two isotopes, but in a recent paper he reported them present in small intensity. So if one looks only for the possible population of neutron shells and for quantum rules controlling them, one should consider the missing isotopes more as an intensity problem.

Until the table of isotopes is completed by a table of their exact atomic weights to 3 decimals, it is rather precarious to generalize the idea that *the smallest isotope represents all neutrons in inner shells, and the largest isotope an additional complete outer shell.* This idea may be justified for the group of elements in Table II, since for those of them which are measured the mass defects certainly increase in equal steps, with the step magnitude 0.008 and 0.009. From mere energetic considerations one should expect that the incorporation of the neutrons takes place with decreasing energy steps, until the last neutron is bound with nearly no energy and bars the incorporation of more neutrons. This helps the conclusion that the neutrons are arranged in shells like the outer electrons, subject to Pauli's exclusion principle and Fermi statistics.[3] At the same time one expects for the α-particles, since they consist of an even number of components, *Bose* statistics and no shell structure at all.

Note added in proof: After this paper was sent in, I received an article of E. N. Gapon[4] being rather identical with the contents of Sections I, II and III of the present paper. Compare also with D. Iwanenko[5] who first suggested the nuclear model used here. One may consider, then, these parts as an introduction into Part II.

[3] J. H. Bartlett, Phys. Rev. **41**, 370 (1932); **42**, 145 (1932).

[4] E. N. Gapon, Zeits. f. Physik **79**, 676 (1932).

[5] D. Iwanenko, Comptes Rendus **195**, 439 (1932).

Neutrons in the Nucleus. II

ALFRED LANDÉ, *Mendenhall Laboratory, Ohio State University*

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In Part I we came to the conclusion, that in several cases the *lightest* isotope of an element represents an arrangement of neutrons in more or less closed shells, that the heavier isotopes indicate the attachment of one neutron after the other, until with the *heaviest* isotope a new outer shell is completed. In the present paper we account for the number of neutrons in the nuclei by the following model. Up to $Z=16$ the neutrons populate a first shell with at most two neutrons. From $Z=17$ to 28 an additional shell of four neutrons is allowed. From $Z=32$ to 36 we see the presence of neutrons in a third shell of eight. It is necessary to assume that between $Z=36$ and 40 the inner shells are filled in with two more neutrons, and the same between $Z=50$ and 54. Evidence for this filling in is seen in certain significant features of the binding energy. It is pointed out that the intensity distribution of the isotopes points to their stability with respect to α and β transformations. This can be used to give a more rational basis to the art of predicting missing isotopes.

I.

USING the scheme "nucleus = α-particles + neutrons + zero or one free proton" in the case of an even or odd charge number, we have plotted in Fig. 1 the number of neutrons in the isotopes against the charge number $Z=1$ to 92 of the elements as far as known. The result can be described as follows (compare with the schematic diagram of Fig. 2). Up to $Z=16$ the number n of neutrons varies between 0 and 2. From $Z=17$ to 28 the number n runs from 0 to 2 to 6. From 32 to 36 we have n between 6 and 14. From 40 to 42 n is found between 8 and 16. The element $Z=50$ has n from 12 to 24, and in $Z=54$ n runs from 16 to 28. The significant feature of this distribution is found in the fact, that the upper and lower limit of the n-range remain constant through a series of Z-values, and then jump up suddenly by several units. In some cases the former n-maximum becomes now n-minimum.

We can account for this numerical arrangement by the model of Fig. 2. Up to $Z=16$ the neutrons populate a first shell with at most 2 neutrons. From $Z=17$ to 28 an additional shell of 4 neutrons is allowed. In $Z=32$ to 36 we see the presence of neutrons in a third shell of 8. It is not meant that these shells are already complete. On the contrary we have to assume (verification in Section II), that between $Z=36$ and 40 the inner shells are filled in with 2 more neutrons, so that the third shell of 8 neutrons rests now on 8

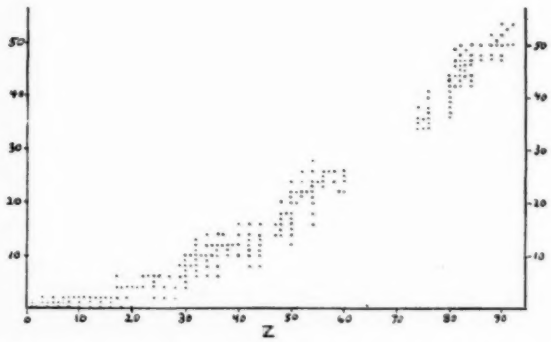

FIG. 1. Number of neutrons in the isotopes as a function of atomic number.

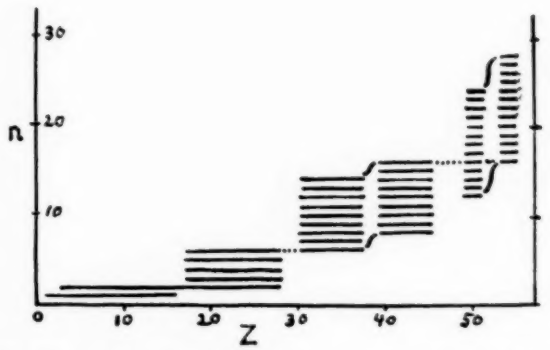

FIG. 2. Idealized schematic diagram corresponding to Fig. 1.

[1] The *odd* elements give mass defects a little *above* our smooth curves $n=$ const., if we calculate Δm by the scheme nucleus = α-particles + neutrons + proton, and a little *below* the curves in the scheme "neutrons + protons." This shows that one of the α-particles has a looser structure inside the nucleus than when isolated.

instead of $2+4=6$ inner neutrons. With $Z=50$ we meet a fourth shell of 12 neutrons built on the former three shells diminished by 4 neutrons. But with $Z=54$ these 4 neutrons are filled in again (see Section II), and the fourth shell is based now on 16 inner neutrons. The observations of isotopes for higher Z are too incomplete to draw conclusions from them.

Altogether we obtain for the elements up to $Z=54$ a table of their *capacity* for neutrons, (Table I) not made use of in the case of "missing" isotopes.

TABLE I. *Neutron shells.*

Z	Neutron shells
3–16	2
20–28	2 4
32–36	2 4 8
40–44	2 6 8
50	2 6 4 12
54	2 6 8 12

Our taking recourse to the assumption of inner shells being filled in seems to render the result very hypothetical indeed. It is with the help of energy considerations that this structure scheme can be verified in an independent way.

II.

In Part I we calculated the mass defects Δm of the isotopes derived from their measured atomic weights according to the scheme nucleus $=\alpha$-particles+neutrons+zero or one proton. If we join by a curve the mass defect dots in Fig. 1 of Part I belonging to a certain *constant* number n, these curves will represent the energy of binding a constant number n of neutrons to a varying number $Z/2$ of α-particles, considering only the *even*[1] elements. Although there are not many dots on each particular curve $n=$const., that are obtained from direct measurements of the exact atomic weights, we know from Part I, that these curves run nearly parallel at constant distances from each other throughout the periodic system.[2] This enables us to extrapolate these curves in a rather wide range with good reason. The result is shown for the even

[2] This fact was first found by E. N. Gapon, Zeits. f. Physik **79**, 676 (1932).

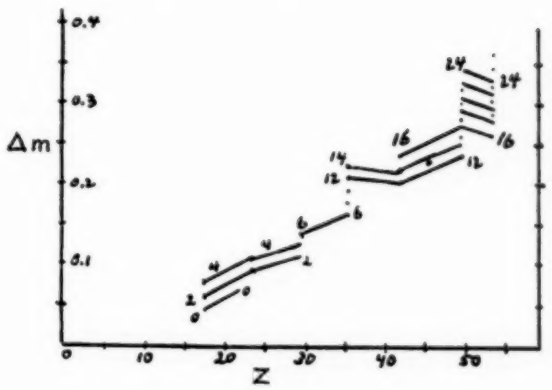

FIG. 3. Mass defect for constant n as a function of Z.

elements in Fig. 3. In general the mass defect Δm increases with increasing number of α-particles attached to a constant number n of neutrons. Only between $Z=36$ and 40 and between $Z=50$ and 54 the curves are descending. These are just the ranges, where the numerical distribution of the isotopes suggested the assumption of *neutrons being filled into inner shells*. We have to interpret the descending parts of the curves $n=$const. as a sign, that the uniform process of attaching α-particles to a fixed number of neutrons is interrupted here. Namely α-particles are apparently bound in these ranges looser than in the preceding ones, as if they were attached more toward the outside of the nucleus, and some of the neutrons were shifted to inner shells. One could try to explain the stability against α-emission on a descending part of the Δm-curve by the assumption that an emission of an outside α-particle would leave the nucleus in a state of excitation with a Δm smaller than the measured Δm of the *stable* product after such an emission.

The extrapolation of our mass defect curves $n=$const. into the unexplored range $Z=54$ to 80 shows that corresponding descending parts must occur here, too, in order to join the curves onto the measured mass defect dots of $Z=80$.

III.

The isotopes of one element, though differing only by the number of neutrons in the outer shell, cannot be supposed to be in a state of mutual equilibrium. Else we should expect to

find a maximum abundance for a certain isotope and a uniform decrease of the intensity to both heavier and lighter isotopes of the same element. Instead we find that the relative abundance varies in large steps up and down, as in the instance of $Z=54$:

$m=$	112	113	114	115	116	117	118	119	120	121	122	123	124
Intens.	0.1	0	0.1	0	2.3	27.1	4.2	20.7	26.4	0	10.3	0	8.8

Only if we consider the 4 families $m=4N$, $4N+1$, $4N+2$, $4N+3$ separately:

112	116	120	124	113	117	121	114	118	122	115	119	123
0.1	2.3	26.4	8.8	0	27.1	0	0.2	4.2	10.3	0	20.7	0

then we obtain a uniform decrease on both sides of the maximum abundance. This indicates of course, that the intensity distribution can only be understood from the historical point of view of α- and β-disintegration or synthesis. For this reason we think that speculations about the formation of nuclei by successive addition of protons and neutrons have not much significance. For every charge number Z there should be a certain number n of neutrons possessing the largest stability, and the stability maximum should run along a uniformly ascending curve in the (nZ)-diagram, smoothing out the corners of Fig. 2. From this point of view one can understand the abundance distribution of the isotopes of each radioactive family separately. In particular the isotopes represented by convex corners of the (nZ)-diagram are extremely weak or even missing, indeed.

Although the members of one family have mass differences of 4 units for a given charge number, the even families $4N$ and $4N-2$ contribute in many cases 2 or even 3 members to the isotopes of one element. These belong to different branches of the family because of forking processes, familiar in the case of radioactive elements. The odd families $4N-1$ and $4N-3$ are, with a few exceptions, represented by only *one* isotope in each element. Forking seems to be much rarer here. Consequently there is no great chance of predicting missing isotopes in the odd families. Furthermore, according to the rule obtained in Section IV, Part I, there is no chance to find stable isotopes of odd charge number with even mass numbers, except for the first elements.

A method of prediction based on the descendence theory has to consider two separate cases. *Either* the present abundance of the "stable" elements and their isotopes is the effect of a *decay* process. Then one will predict missing isotopes on the *heavier* end of the mass spectrum of some elements. For instance, one will predict the missing isotopes $n=6$ in $Z=26$ and 28, since $n=6$ in $Z=24$ can be reached by α-disintegration only through the two missing isotopes, if one wants to avoid too large detours from the intensity maximum. *Or* the present abundance is the result of α- and β-*synthesis*. Then one will predict missing isotopes on the *lighter* end of the mass spectrograms of some elements. It would be interesting to tell from a more completed table of isotopes, whether the present state appears to be the result of decay or synthesis.

The Vector Model and the Pauli Principle

M. H. JOHNSON, JR.,* *New York University*

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The vector model is examined in the light of the quantum theory of wave fields. First the distributions of electrons among the electronic states are limited to correspond to the atomic states arising from one electronic configuration. A set of independent angular momentum vectors $\mathbf{l}_1$, $\mathbf{l}_2$, $\cdots\mathbf{s}_1$, $\mathbf{s}_2\cdots$ is found, in which one orbital and one spin vector are associated with each group of electronic states, rather than individual electrons, having given values of the quantum numbers n and l. Any other vector $\mathbf{T}$ may be decomposed into a sum of independent vectors $\mathbf{t}_i$, one associated with each of the same group of electronic states. The usual commutation relations obtain among the vectors $\mathbf{t}_i$, $\mathbf{l}_i$ and $\mathbf{s}_i$. On further limiting the distributions to correspond to atomic states arising from electronic configurations containing no equivalent electrons, it is shown that the matrix of $\Sigma_k f(\mathbf{l}_k^0, \mathbf{s}_k^0)$ (an operator in coordinate space in which f is any algebraic function of the components of $\mathbf{l}$ and $\mathbf{s}$) can be constructed from the vectors $\mathbf{l}_1$, $\mathbf{l}_2$, $\cdots\mathbf{s}_1$, $\mathbf{s}_2$, $\cdots$ according to the usual laws of matrix mechanics.

IN previous papers[1] a method of calculating the matrix $H_1=\sum_k a_k\mathbf{l}_k\cdot\mathbf{s}_k$ for any electronic configuration has been described. Here it was assumed that; (1) $\mathbf{l}_1\cdots\mathbf{l}_n\mathbf{s}_1\cdots\mathbf{s}_n$ constitute a set of independent angular momentum vectors satisfying the usual commutation relations. (2) the total orbital angular momentum $\mathbf{L}$ is given by

$$\mathbf{L}=\sum_k\mathbf{l}_k \tag{1}$$

and the total spin $\mathbf{S}$ by

$$\mathbf{S}=\sum_k\mathbf{s}_k\,. \tag{2}$$

This method enables one to obtain the matrix H_1 in any representation described by giving definite values to J^2 ($\mathbf{J}=\mathbf{L}+\mathbf{S}$), L^2 and S^2 and by assigning a definite structure to the $\mathbf{l}$ vectors and to the $\mathbf{s}$ vectors. It could easily be generalized to give this matrix in a representation described by any definite structure of the vectors $\mathbf{l}_1\cdots\mathbf{l}_n\mathbf{s}_1\cdots\mathbf{s}_n$.

In the above references the results of applying this method were directly used to obtain the matrix of the spin-orbit interaction for various electronic configurations. Obviously some proof is needed to justify this step for it is not at all self-evident that any such set of vectors as $\mathbf{l}_1\cdots\mathbf{l}_n\mathbf{s}_1\cdots\mathbf{s}_n$ can be found when the Pauli principle is correctly taken into account. We are naturally led to a more general question. In view of the Pauli principle which requires that all electrons be identical in nature, what meaning can be ascribed to the vector model of an atomic configuration? The point has already been considered by von Neuman and Wigner[2] who, in their discussions of vector coupling, take account of the symmetrization of the wave functions required by the Pauli principle. More recently Shortley[3] has justified the specific applications made in reference 1 in a similar way. Nevertheless we propose an examination of this question from a different point of view which is more directly concerned with the vector model itself. Whereas these authors use wave functions derived from an analysis of vector coupling and then symmetrized for the Pauli principle, we shall employ a formulation of the problem embodying the Pauli principle at the outset and shall find therein the constituents of a vector model.

For this purpose the quantum theory of wave fields[4] is convenient. Then if

$$X^0=\sum_k X^0(x_k) \tag{3}$$

* National Research Fellow.

[1] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931); ibid. **39**, 197 (1932).

[2] J. v. Neumann and E. Wigner, Zeits. f. Physik **49**, 73 (1928).

[3] G. H. Shortley, Phys. Rev. **40**, 185 (1932).

[4] P. A. M. Dirac, Proc. Roy. Soc. (London) **A114**, 243 (1927); P. Jordan u. O. Klein, Zeits. f. Physik **45**, 751 (1927); P. Jordan, ibid. 766 and **44**, 473 (1927); Jordan u. Wigner, ibid. **47**, 631 (1928); Fock, ibid. **75**, 622 (1932).

is an Hermitean operator in coordinate space,[5] it will be represented by

$$X=\sum_{pr}a_p^+a_r(p|X^0|r) \tag{4}$$

in the space of the N_r's (N_r = the number of electrons in the state r). Here

$$(p|X^0|r)=\int u_p^*(x)X^0(x)u_r(x)dx=(r|X^0|p)^*. \tag{5}$$

Similarly if

$$W^0=\sum_{k>l}W^0(x_k,x_l),\quad W^0(x_k,x_l)=W^0(x_l,x_k) \tag{6}$$

is an Hermitean operator in coordinate space, it will be represented in the space of the N_r's by

$$W=\tfrac{1}{2}\sum_{pqrs}a_p^+a_q^+a_sa_r(pq|W^0|rs), \tag{7}$$

where

$$(pq|W^0|rs)=\int u_p^*(x_1)u_q^*(x_2)W^0(x_1,x_2)u_r(x_1)u_s(x_2)dx_1dx_2=(qp|W^0|sr)=(rs|W^0|pq)^*. \tag{8}$$

Here the u's form a complete set of solutions of a central field problem yielding definite values for the projections of the orbital and spin momentum along the z axis. The summation indices range over all the electronic states of this central field problem. The a's are the noncommutative amplitudes which operate on the variables N_r and satisfy the well-known exchange relations

$$\begin{gathered}a_p^+a_r+a_ra_p^+=\delta_{pr},\quad a_p^+a_r^++a_r^+a_p^+=0,\\ a_pa_r+a_ra_p=0.\end{gathered} \tag{9}$$

They have the following operational formulation.[6]

$$\begin{aligned}a_r^+&=N_r\Delta_r\nu_r=-N_r\nu_r\Delta_r=\Delta_r(1-N_r)\nu_r,\\ a_r&=\nu_r\Delta_rN_r=-\Delta_r\nu_rN_r=(1-N_r)\nu_r\Delta_r,\end{aligned} \tag{10}$$

where Δ_r operating on a function of N_r changes N_r to $1-N_r$ and ν_r is the sign function $\Pi_{i=1}^{r}(1-2N_i)$. It is clear that

$$a_r^+a_r=N_r,\quad a_ra_r^+=1-N_r. \tag{12}$$

As a consequence of the exchange relations satisfied by the a's, the N's commute among themselves and have the eigenvalues 0 and 1. We shall also need the following commutation relation which is easily obtained from Eq. (9). If Y is an operator similar to X

$$[X,\ Y]=\sum_{pr}a_p^+a_r(p|[X^0,\ Y^0]|r), \tag{13}$$

where

$$\begin{aligned}&(p|[X^0,\ Y^0]|r)\\ &\quad=\sum_s[(p|X^0|s)(s|Y^0|r)-(p|Y^0|s)(s|X^0|r)].\end{aligned}$$

We shall use this relation in special cases in which at least one of the matrices X or Y is diagonal in some quantum number. For example X may be diagonal in the inner quantum number j but not in the magnetic quantum number. Then it is convenient to write $X=\sum_jX_j$ and $Y=\sum_jY_j+\sum_{jj'}Y_{jj'}$. For each X_j and Y_j the indices p, r cover the range of different magnetic quantum numbers belonging to the same j. We can calculate $[X_j,\ Y_j]$ in the same way as Eq. (13) and the summation over s will then be limited to the subgroup of states having the same j. As long as at least one of the matrices X or Y is diagonal in j, this sum will still be equal to $(p|[X^0,\ Y^0]|r)$. This fact will be used in obtaining Eqs. (18), (19) and (23).

As the N's commute among themselves, they may all be simultaneously diagonal. A physical state of the atom can be described by assigning the value 0 or 1 to each N, that is by giving the distribution of electrons among the electronic states. Thus we might have one electron in the electronic state 1, one electron in the electronic state 3 and no electrons in all other electronic states. The eigenfunction in the space of the N_r's for this state will be just the product of a number of δ functions $\delta(1,\ N_1)\delta(0,\ N_2)\delta(1,\ N_3)\ \delta(0,\ N_4)\cdots$, where each δ function is analogous to the familiar spin function (because N_r, like the spin variable, has only two possible values). With a set of such eigenfunctions, the matrix of any operator in the space of the N_r's may be constructed in the usual manner. On the other hand we know that the above atomic state

[5] The superscript ^{0} is used to distinguish operators in coordinate space from matrices and operators in the space of the N_r's.

[6] W. Heisenberg, Ann. d. Physik **10**, 888 (1931).

can be equally well described in configuration space by the antisymmetric eigenfunction

$$\begin{vmatrix} u_1(x_1) & u_3(x_1) \\ u_1(x_2) & u_3(x_2) \end{vmatrix}.$$

The matrix of any operator in configuration space can readily be constructed from such a set of antisymmetric eigenfunctions. Since the formulation of a problem in terms of quantized amplitudes is mathematically equivalent to its formulation in configuration space with antisymmetric eigenfunctions, the matrix of any operator constructed from eigenfunctions in the space of the N_r's is exactly equivalent to the matrix of the same operator constructed from antisymmetric eigenfunctions in configuration space.

The problem of obtaining the eigenvalues of H, the Hamiltonian operator expressed in terms of quantized amplitudes, is equivalent to an exact solution of the Schrödinger equation with antisymmetric wave functions. Just as it is convenient to solve the Schrödinger equation considering a limited group of atomic states, so it is here convenient to consider together a correspondingly limited number of distributions of electrons among the electronic states. With this in mind we divide all the electronic states r into a number of subgroups i according to the different values of the quantum numbers $n_i l_i$. In each subgroup there will be $2(2l_i+1)$ electronic states corresponding to the projections of l_i and the spin along the z axis. Let M_i be the number of electrons in the subgroup i.

$$\begin{gathered} M_i=\sum_p(i)N_p=\sum_{pr}a_p{}^+a_r(p\,|\,M_i\,|\,r), \\ (p\,|\,M_i\,|\,r)=\delta_{pr}\delta_i{}^r, \end{gathered} \tag{14}$$

where $\sum_p(i)$ means a summation limited to the states of the subgroup i and $\delta_i{}^r$ is a function which vanishes unless r is in the subgroup i in which case it has the value 1. We will consider together distributions of electrons among the electronic states for which M_1, M_2, etc., have fixed values. These distributions correspond to the states of an electronic configuration in which there are M_1 equivalent electrons with $nl=n_1l_1$, M_2 equivalent electrons with $nl=n_2l_2$, etc.

Let us see what restrictions the constancy of $M_1, M_2, \cdots$ places on an operator X which may occur in the Hamiltonian. For M_i to have a definite value it is necessary that

$$[X, M_i]=0. \tag{15}$$

On employing Eqs. (13) and (14) the condition becomes

$$(p\,|\,X^0\,|\,r)(\delta_i{}^r-\delta_i{}^p)=0.$$

To insure that this equation is fulfilled for all i we must omit all terms from $\sum_{pr}a_p{}^+a_r(p\,|\,X^0\,|\,r)$ except those for which p and r lie in the same subgroup. Hence

$$X=\sum_iX_i, \quad X_i=\sum_{pr}(i)a_p{}^+a_r(p\,|\,X^0\,|\,r). \tag{16}$$

To see with what matrix components the omitted terms in Eq. (16) are connected, consider $a_p{}^+a_r$ when p and r are in different subgroups i and j, respectively. From Eq. (10) it is clear that $a_p{}^+a_r$ operating on an eigenfunction consisting of a product of δ functions, gives rise to a new eigenfunction obtained from the first by removing an electron from the state r of the subgroup j and placing it in the state p of the subgroup i. Thus such terms are connected with the matrix components between different electronic configurations. The omission of these terms is precisely equivalent to a first order perturbation theory for the Schrödinger equation which considers together only those states arising from a single electronic configuration.

We now fix our attention on the angular momentum operators. By Eq. (16) we have

$$\mathbf{L}=\sum_i\mathbf{l}_i, \quad \mathbf{l}_i=\sum_{pr}(i)a_p{}^+a_r(p\,|\,\mathbf{l}^0\,|\,r). \tag{17}$$

We note that every component of $\mathbf{l}_i$ commutes with every component of $\mathbf{l}_j (i\neq j)$ as a result of the exchange relations satisfied by the a's. From Eq. (13) and the remark following it, we have

$$\mathbf{l}_i\times\mathbf{l}_i=\sum_{pr}(i)a_p{}^+a_r(p\,|\,\mathbf{l}^0\times\mathbf{l}^0\,|\,r).$$

But $\mathbf{l}^0\times\mathbf{l}^0=i\mathbf{l}^0$; so we find

$$\mathbf{l}_i\times\mathbf{l}_i=i\mathbf{l}_i. \tag{18}$$

In a similar way it may be shown

$$\begin{gathered} \mathbf{S}=\sum_i\mathbf{s}_i, \quad \mathbf{s}_i=\sum_{pr}(i)a_p{}^+a_r(p\,|\,\mathbf{s}^0\,|\,r), \\ \mathbf{s}_i\times\mathbf{s}_i=i\mathbf{s}_i. \end{gathered} \tag{19}$$

Also we find that every component of $\mathbf{s}_i$ com-

mutes with $\mathbf{s}_j (i \neq j)$ and with all components of $\mathbf{l}_k$ (where k may be equal to i).

By this decomposition of the total angular momenta we have found a set of independent angular momentum vectors $\mathbf{l}_1, \mathbf{l}_2, \cdots, \mathbf{s}_1, \mathbf{s}_2, \cdots$, one orbital and one spin vector being associated with each subgroup i, which have the correct commutation properties. Before the formulation of the Pauli principle with antisymmetric wave functions one could speak of the n'th electron, as distinguished by the coordinates x_n, as having a certain angular momentum. When antisymmetric wave functions are introduced, the possibility of distinguishing an electron by its coordinates is lost so this manner of speaking is no longer correct. Nevertheless vector model considerations are still valid if we understand by such an expression as "the angular momentum of a d electron," an angular momentum vector associated with the d electronic states rather than with some electronic coordinates. It should be observed that we have succeeded in finding only two vectors $\mathbf{l}_i$ and $\mathbf{s}_i$ belonging to the subgroup i. If $M_i = 3$ (say), meaning there are three equivalent electrons with $nl = n_i l_i$, we are justified in speaking of "the angular momentum of the shell of three electrons" but we have not found anything that corresponds to the angular momenta of the individual electrons in this shell.

It is of interest to find the commutation relations of other vectors with the angular momenta. Suppose

$$\mathbf{T}^0 = \sum_k \mathbf{t}^0(x_k) \tag{20}$$

is a vector in coordinate space which satisfies the usual commutation relations

$$[l_x^0, t_x^0] = 0, \quad [l_x^0, t_y^0] = [t_x^0, l_y^0] = i t_z^0. \tag{21}$$

Then by Eq. (16)

$$\mathbf{T} = \sum_i \mathbf{t}_i, \quad \mathbf{t}_i = \sum_{pr}(i) a_p^+ a_r (p | \mathbf{t}^0 | r). \tag{22}$$

Here $\mathbf{t}_i$ is an independent vector in the sense that it commutes with all components of $\mathbf{t}_j$, $\mathbf{l}_j$ and $\mathbf{s}_j (i \neq j)$. Eq. (13) yields

$$[l_{xi}, t_{yi}] = \sum_{pr}(i) a_p^+ a_r (p | [l_x^0, t_y^0] | r).$$

Then because of Eq. (21)

$$[l_{xi}, t_{yi}] = i t_{zi}. \tag{23}$$

We therefore see that $\mathbf{t}_i$, $\mathbf{l}_i$ and $\mathbf{s}_i$ satisfy the same commutation relations as $\mathbf{t}^0$, $\mathbf{l}^0$ and $\mathbf{s}^0$.

Finally let $F^0 = \sum_k f(\mathbf{l}_k^0, \mathbf{s}_k^0)$, where $f(\mathbf{l}^0, \mathbf{s}^0)$ is any function built up by algebraic processes from the components of $\mathbf{l}^0$ and $\mathbf{s}^0$. We decompose F by Eq. (16). $F = \sum_i F_i$. We now limit the values of M_i to one or zero which means that we are dealing exclusively with electronic configurations containing no equivalent electrons. We propose to show that with this restriction

$$F_i = f(\mathbf{l}_i, \mathbf{s}_i). \tag{24}$$

Suppose Eq. (24) is true for two functions G and H. Then it is true for their sum (for brevity we write g^0 for $g(\mathbf{l}^0, \mathbf{s}^0)$ and h^0 for $h(\mathbf{l}^0, \mathbf{s}^0)$) for we have

$$(G+H) = \sum_i (G+H)_i,$$
$$(G+H)_i = \sum_{pr}(i) a_p^+ a_r (p | g^0 + h^0 | r) = G_i + H_i$$

from which the desired result follows immediately. Next consider the product

$$\begin{aligned} (GH) &= \sum_i (GH)_i, \\ (GH)_i &= \sum_{pr}(i) a_p^+ a_r (p | g^0 h^0 | r). \end{aligned} \tag{25}$$

Because of the limitation of M_i to the values zero or one, we are dealing with at most one electron in the subgroup i. For this reason any operator representing the interaction of two electrons in the subgroup i must vanish identically. Thus, in particular,

$$\sum_{pqrs}(i) a_p^+ a_q^+ a_s a_r (p | g^0 | r)(q | h^0 | s) = 0. \tag{26}$$

As this is an essential point in the argument, let us consider it in a little more detail. From the fact that $a_r a_r = 0$ we find $a_r(1 - N_r) = 0$, $N_r a_r = 0$ or if r is in the subgroup i $a_r M_i = (1 + M_i) a_r$. Now let M_i be a variable so that $\delta(M_i', M_i) f$ represents a state in which there are M_i' electrons in the subgroup i. Here f is some function of the N's in the subgroup i which gives the distribution of electrons among the states of the subgroup. Then

$$\begin{aligned} a_r \delta(M_i', M_i) &= \delta(M_i', M_i + 1) a_r \\ &= \delta(M_i' - 1, M_i) a_r. \end{aligned}$$

Thus the effect of commuting a_r through the δ function is to decrease the number of electrons in the subgroup i by 1. If $M_i=1$, the result of commuting $a_s a_r$ through the δ function is plainly zero so that in this case such an operator as $\sum_{pqrs}(i)a_p{}^+a_q{}^+a_s a_r(pq|A|rs)$ always yields zero when applied to an eigenfunction in the space of the N's. Returning to Eq. (26), if the order of the a's is changed, it is readily found that

$$G_i H_i=\sum_{pqrs}(i)a_p{}^+a_r a_q{}^+a_s(p|g^0|r)(q|h^0|s)$$
$$=\sum_{prs}(i)a_p{}^+a_r(p|h^0|s)(s|g^0|r)=(GH)_i.$$

It immediately follows if Eq. (24) is true for G and H, it is true for their product (GH), Eq. (24) is surely satisfied if g^0 and h^0 equal any of the components of $\mathbf{l}^0$ and $\mathbf{s}^0$. Consequently it is true for any function built up by algebraic processes from these components.

In particular let

$$H^0=\sum_k V(r_k{}^0)\mathbf{l}_k{}^0\cdot\mathbf{s}_k{}^0,$$
$$H_i=\sum_{pr}(i)a_p{}^+a_r(p|V(r^0)\mathbf{l}^0\cdot\mathbf{s}^0|r). \tag{27}$$

Here $V(r)$ is independent of the projections of the momentum vectors along the z axis so

$$(p|V(r^0)\mathbf{l}^0\cdot\mathbf{s}^0|r)=a_i(p|\mathbf{l}^0\cdot\mathbf{s}^0|r),$$

where a_i is the integral of $V(r)$ over the radial part of the wave functions u for the subgroup i. Hence

$$H_i=a_i\sum_{pr}(i)a_p{}^+a_r(p|\mathbf{l}^0\cdot\mathbf{s}^0|r)=a_i\mathbf{l}_i\cdot\mathbf{s}_i. \tag{28}$$

Thus we see in this case of an electronic configuration containing no equivalent electrons we are completely justified in building up the matrix of the spin-orbit interaction from the vectors $\mathbf{l}_1, \mathbf{l}_2, \cdots \mathbf{s}_1, \mathbf{s}_2, \cdots$ according to the usual laws of matrix calculus.

Note on Almost Closed Shells

M. H. JOHNSON, JR.,* *Department of Physics, New York University*

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Heisenberg's treatment of an almost closed shell is extended to electronic configurations consisting of several almost closed shells plus other electrons not in the shells. In this way Shortley's results are obtained with additional information about the nondiagonal matrix elements of the electrostatic energy. The results of calculating the electrostatic energies by this method are presented for the configurations p^5p, d^9d and d^9p.

HEISENBERG[1] has treated an almost closed shell by means of the quantum theory of wave fields. He considers those terms in the energy operator which are connected with atomic states arising from a configuration of equivalent electrons. He then changes from the variables N_r (the number of electrons in the state r) to the variables $\overline{N}_r=1-N_r$ (the number of "holes" in the state r). Corresponding to the transformed energy operator there is a Schrödinger equation in a configuration space whose coordinates are connected with the electrons missing from the shell. The results he obtains for atomic spectra and the anomalous Hall effect follow from this equation.

More recently Shortley[2] has considered in atomic spectra the more general problem of an electronic configuration consisting of an almost complete shell plus other electrons not belonging in the shell. In calculating diagonal elements of the electrostatic energy matrix he showed how the sums which occur over the electrons in the shell may be replaced by sums over the electrons missing from the shell. His formulas may be interpreted by saying that so far as the diagonal electrostatic energy matrix elements go, the missing electrons interact with each other and with other electrons as though they were positively charged. The formulas which he obtains for the matrix of the spin-orbit interaction may be interpreted similarly, for if the missing electrons act as though positively charged, the portion of the spin-orbit interaction connected with them is reversed in sign. He also showed that in working out the M_L and M_S values belonging to the different atomic states (eigenvalues of L_z and S_z, respectively) the m_l and m_s associated with each missing electron must be taken with a negative sign.

It is the purpose of this note to point out that these results can be obtained rather nicely from the method Heisenberg used for an almost closed shell alone. Our procedure will differ slightly from that of Heisenberg in that we will not pass from the variables $\overline{N}_r$ to a Schrödinger equation. Rather we will interpret operators in terms of these variables through their matrices, a method which naturally suggests itself as a result of the discussion on pages 628 and 629 of the preceding paper.

As before, by assigning definite values to all the M_i (the number of electrons in a shell i) we limit the distributions of electrons among the electronic states to correspond to all the atomic states arising from one electronic configuration. Our Hamiltonian is of the form

$$H=H^1+H^2, \quad H^1=\sum_{pr}a_p^+a_r(p|H^1|r), \qquad H^2=\tfrac{1}{2}\sum_{pqrs}a_p^+a_q^+a_sa_r(pq|H^2|rs), \tag{1}$$

where we take H^1 to be the spin-orbit interaction and H^2 the electrostatic repulsion of the electrons. In order that all the M_i have definite values, by Eq. (19) of the preceding paper we have

$$H^1=\sum_iH_i, \quad H_i=\sum_{pr}(i)a_p^+a_r(p|H^1|r). \tag{2}$$

We must see what is required of H^2 in order that all the M_i have definite values. Now

* National Research Fellow.

[1] W. Heisenberg, Ann. d. Physik **10**, 888 (1931).

[2] G. H. Shortley, Phys. Rev. **40**, 185 (1932).

$$[H^2, M_i]=\tfrac{1}{2}\sum_{pqrst}[a_p^+a_q^+a_sa_r, N_t]\delta_i^t(pq|H^2|rs).$$

From the commutation relations among the a's we find

$$a_pN_t-N_ta_p=\delta(p,t)a_t, \qquad a_p^+N_t-N_ta_p^+=-\delta(p,t)a_t^+.$$

Hence

$$[H^2, M_i]=-\tfrac{1}{2}\sum_{pqrs}a_p^+a_q^+a_sa_r(pq|H^2|rs)(\delta_i^p+\delta_i^q-\delta_i^r-\delta_i^s). \tag{3}$$

Therefore in order to have $[H_1^2M_i]=0$ we retain in H^2 only terms for which r or s is in the subgroup i if p is in i or if q is in i, or for which all four indices are in i. Hence we may write

$$\begin{aligned}H^2&=\sum_iH_{ii}+\sum_{i>j}H_{ij}, \qquad H_{ii}=\tfrac{1}{2}\sum_{pqrs}(i)a_p^+a_q^+a_sa_r(pq|H^2|rs),\\ H_{ij}&=\sum_{pr}(i)\sum_{qs}(j)a_p^+a_q^+a_sa_r[(pq|H^2|rs)-(pq|H^2|sr)].\end{aligned} \tag{4}$$

Now suppose in subgroups 1 and 2 we have almost closed shells so that it is advantageous to transform to the missing electrons in these subgroups. We use the variables $\bar{N}_r=1-N_r$ if r is in subgroup 1 or 2; $\bar{N}_r=N_r$ if r is not in subgroup 1 or 2. Then according to Heisenberg

$$\begin{aligned}&\bar{a}_r^+=a_r \text{ and } \bar{a}_r=a_r^+ \text{ if } r \text{ is in subgroup 1 or 2}\\ &\bar{a}_r^+=a_r^+ \text{ and } \bar{a}_r=a_r\\ &\qquad\qquad \text{if } r \text{ is not in subgroup 1 or 2.}\end{aligned} \tag{5}$$

The $\bar{a}$'s obey exactly the same commutation relations as the a's.

Consider first the spin-orbit interaction. If $i=1$ or 2, H_i transforms just as in Heisenberg's case. If i refers to some other subgroup, H_i is unchanged by the transformation. Thus

$$\begin{aligned}&\bar{H}^1=\sum_i\bar{H}_i,\\ &\bar{H}_i=-\sum_{pr}(i)\bar{a}_p^+\bar{a}_r^+(p|H^1|r)^*, \quad i=1, 2,\\ &\bar{H}_i=\sum_{pr}(i)\bar{a}_p^+\bar{a}_r(p|H^1|r), \quad i>2.\end{aligned} \tag{6}$$

Here we have omitted a term which is the same for all our distributions and represents the magnetic energy of the closed shells 1 and 2. Also we have used the fact $(r|H^1|p)=(p|H^1|r)^*$.

Consider next the electrostatic interaction. The terms $H_{11}+H_{22}+H_{21}$ transform just as in Heisenberg's case. The terms H_{ii} $i>2$ and H_{ij} $i>j>2$ are unchanged. There remain the terms H_{ij} $i>2$, $j=1, 2$ which on using Eq. (5) become

$$\begin{aligned}\bar{H}_{ij}&=\sum_{pr}(i)\sum_{qs}(j)\bar{a}_p^+\bar{a}_q\bar{a}_s^+\bar{a}_r[(pq|H^2|rs)-(pq|H^2|sr)]\\ &=-\sum_{pr}(i)\sum_{qs}(j)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r[(ps|H^2|rq)-(ps|H^2|qr)].\end{aligned}$$

A constant term representing the interaction of the electrons in the subgroup i with the closed shell j has been omitted. The first integral in the above expression can be brought in the convenient form $(pq|H^2|rs)$ by using the complex conjugate wave functions for the "holes." However, this does not help with the second integral so we leave it as above. Dropping constant terms we have

$$\begin{aligned}&\bar{H}^2=\sum_i\bar{H}_{ii}+\sum_{i>j}H_{ij},\\ &\bar{H}_{ii}=\tfrac{1}{2}\sum_{prqs}(i)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r(pq|H^2|rs)^*, \quad i=1, 2,\\ &\bar{H}_{ii}=\tfrac{1}{2}\sum_{pqrs}(i)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r(pq|H^2|rs), \quad i>2,\\ &\bar{H}_{21}=\sum_{pr}(2)\sum_{qs}(1)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r[(pq|H^2|rs)^*-(pq|H^2|sr)^*],\\ &\bar{H}_{ij}=-\sum_{pr}(i)\sum_{qs}(j)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r[(ps|H^2|rq)-(ps|H^2|qr)], \quad i>2, j=1, 2,\\ &\bar{H}_{ij}=\sum_{pr}(i)\sum_{qs}(j)\bar{a}_p^+\bar{a}_q^+\bar{a}_s\bar{a}_r[(pq|H^2|rs)-(pq|H^2|sr)], \quad i>j>2.\end{aligned} \tag{7}$$

We should also examine the angular momentum operators. We have

$$L_z=\sum_i l_{zi}, \qquad l_{zi}=\sum_{pr}(i)a_p^+a_r(p|l_z|r)=\sum_p(i)N_pm_{lp} \tag{8}$$

and

$$S_z=\sum_i s_{zi}, \qquad s_{zi}=\sum_p(i)N_p m_{sp}. \tag{9}$$

Now

$$\bar{l}_{zi}=-\sum_{pr}(i)\bar{a}_p{}^+\bar{a}_r(p|l_z|r)^*=-\sum_p(i)\bar{N}_p m_{lp}, \quad i=1,2, \qquad \bar{l}_{zi}=\sum_p(i)\bar{N}_p m_{lp}, \quad i>2. \tag{10}$$

Similarly

$$\bar{S}_{zi}=-\sum_p(i)\bar{N}_p m_{sp}, \quad i=1,2, \qquad \bar{S}_{zi}=\sum_p(i)\bar{N}_p m_{sp}, \quad i>2. \tag{11}$$

With the set of eigenfunctions in the space of the N's considered on p. 628 of the previous paper, we could construct the matrix of H^1 and of H^2 before transforming to the holes. According to the discussion of the preceding paper these matrices will be essentially the same as the matrix of H^1 and H^2 constructed with antisymmetric wave functions (Dirac-Slater determinants) in coordinate space. After the transformation the same set of eigenfunctions referred to the variable $\bar{N}_r$ may be used to construct the matrix of $\bar{H}^1$ and $\bar{H}^2$. Now the $\bar{a}$'s bear the same relation to the $\bar{N}$'s as the a's to the N's. Consequently if $\bar{G}$ has the same form in the $\bar{a}$'s as G has in the a's, its matrix may be obtained by comparison[3] with the matrix of G. For example

$$G=\sum_{pqrs}a_p{}^+a_q{}^+a_s a_r(pq|G_0|rs),$$
$$\bar{G}=\sum_{pqrs}\bar{a}_p{}^+\bar{a}_q{}^+\bar{a}_s\bar{a}_r(pq|G_1|rs).$$

Then the matrix of $\bar{G}$ is obtained from the matrix of G by substituting in the latter the elements $(pq|G_1|rs)$ for $(pq|G_0|rs)$.

On comparing Eq. (6) and Eq. (2) and remembering H^1 is a real operator the matrix of the spin-orbit interaction is correctly obtained if we suppose the missing electrons in shells 1 and 2 act as though positively charged so that the part of the spin-orbit interaction associated with the holes is negative in sign. On comparing Eq. (7) with Eq. (4) and remembering H^2 is a real operator the matrix of the electrostatic interaction is correctly obtained on the same assumption if in addition we replace the elements

$$(pq|H^2|rs)-(pq|H^2|sr)$$

which occur in the interaction terms between a hole and an electron, by

$$(ps|H^2|rq)-(ps|H^2|qr).$$

For the diagonal elements ($p=r$, $q=s$) the latter is equal to the former but for the nondiagonal elements it is otherwise. Finally on comparing Eq. (10) with Eq. (8) and Eq. (11) with Eq. (9) we see that the M_L and M_S values of the atomic states are correctly obtained if the m_l and m_s associated with the missing electrons are taken with a negative sign. Thus in the configuration d^9p if $m_l=-2$, $m_s=-\frac{1}{2}$ for the d hole and $m_l=1$, $m_s=\frac{1}{2}$ for the p electron, $M_L=3$ and $M_S=1$.

Appended are the electrostatic energies[4] for the configurations p^5p, d^9d and d^9p as found by making the necessary changes in the calculations for the configurations $p.p$, $d.d$ and $d.p$ by Slater's method.

p^5p

$$^3D=-F_0-F_2, \qquad ^1P=-F_0+5F_2,$$
$$^1D=-F_0-F_2+12G_2, \qquad ^3S=-F_0-10F_2,$$
$$^3P=-F_0+5F_2, \qquad ^1S=-F_0-10F_2+6G_0.$$

d^9d

$$^3G=-F_0-4F_2-F_4,$$
$$^1G=-F_0-4F_2-F_4+140G_4,$$
$$^3F=-F_0+8F_2+9F_4,$$
$$^1F=-F_0+8F_2+9F_4,$$
$$^3D=-F_0+3F_2-36F_4,$$
$$^1D=-F_0+3F_2-36F_4+28G_2,$$
$$^3P=-F_0-7F_2+84F_4,$$
$$^1P=-F_0-7F_2+84F_4,$$
$$^3S=-F_0-14F_2-126F_4,$$
$$^1S=-F_0-14F_2-126F_4+10G_0,$$

[3] The comparison is between the matrix of $\bar{G}$ for a certain electronic configuration and the matrix of G for another electronic configuration obtained from the first by replacing the holes with electrons.

[4] The result for p^5p has already been given by Shortley, reference 2. The notation here used for the F's and G's is that of Condon and Shortley, Phys. Rev. **37**, 1025 (1931).

Added in proof: I am indebted to Professor Van Vleck for informing me that the electrostatic energies for d^9p have been independently calculated by C. W. Ufford whose results agree with those given here.

d^9p

$^3F = -F_0 - 2F_2$, $^1D = -F_0 + 7F_2$,

$^1F = -F_0 - 2F_2 + 90G_3$, $^3P = -F_0 - 7F_2$,

$^3D = -F_0 + 7F_2$, $^1P = -F_0 - 7F_2 + 20G_1$.

Two things are at once apparent. The resonance separations of the singlets and triplets decrease with increasing L values; and starting with the next to the highest L value, the resonance separation for alternate L values is zero. These facts, together with the larger value of the spin-orbit parameter for almost closed shells, explain why intermediate coupling sets in much sooner in the periodic table for closed shells than for the corresponding configurations at the other side of the table.

In conclusion the writer wishes to thank Professor Breit for many very helpful discussions and suggestions on the subject of these two papers.

Nuclear Magnetic Moments

S. GOUDSMIT, *University of Michigan*

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This paper contains approximate formulas (Eqs. (5) and (6)) for the calculation of nuclear magnetic moments from observed hyperfine structure separations.

THE hyperfine splitting of an energy level with total angular momentum $Jh/2\pi$ is governed by the formula

$$\delta\nu = AIJ\cos(IJ)$$
$$= \tfrac{1}{2}A\{F(F+1)-J(J+1)-I(I+1)\},$$

in which I stands for the nuclear moment in units $h/2\pi$, F is the fine structure quantum number, the resultant of I and J, and the cosine is supposed to be a "quantum" cosine. The proportionality factor A depends in a rather complicated way upon the quantum numbers of the energy state under consideration and is furthermore proportional to the nuclear g-value. In the hyperfine splitting A represents the proportionality factor obtained when one applies the interval rule. It is equal to the distance between two adjacent hyperfine levels divided by the largest of their F values and counted positive when the larger F value belongs to the higher energy.

For a single electron one writes a instead of A and in a hydrogenic case the following formula holds:

$$a = \frac{R\alpha^2 Z^3}{n^3(l+\frac{1}{2})j(j+1)}\frac{g(I)}{1838}\text{ cm}^{-1}. \qquad (1)$$

The symbols in this expression have the usual meaning, the nuclear g-value, $g(I)$, is the ratio of the magnetic to the mechanical moment of the nucleus, the former expressed in "proton magnetons" $eh/4\pi Mc$, M being the mass of the proton. In analogy with the electron one expects for a single proton $I=\frac{1}{2}$ and $g(I)=2$.

For a single outer electron in a penetrating orbit one expects that an approximation similar to that derived by Landé for ordinary multiplet separations can be applied here. This gives[1]:

$$a = \frac{R\alpha^2 Z_i Z_o^2}{n_o^3(l+\frac{1}{2})j(j+1)}\frac{g(I)}{1838}\text{ cm}^{-1}. \qquad (2)$$

The derivation of this formula assumes that the properties of the energy state can be considered as arising from two approximately hydrogenic regions of the atom, the outer one with an effective nuclear charge Z_o and a principal quantum number n_o, and the inner one with an average effective nuclear charge Z_i. The value of Z_o is 1 for a neutral atom, 2 for a state of a once ionized atom, etc., n_o is the Rydberg denominator, which can be calculated if the absolute term value is known. The values of Z_i are discussed below.

For non-s electrons the ordinary spin doublets are given by the well-known formula

$$\Delta\nu = \frac{R\alpha^2 Z_i^2 Z_o^2}{n_o^3 l(l+1)}\text{ cm}^{-1}. \qquad (3)$$

Combining this with Eq. (2), assuming that Z_i will have the same value in both formulas, one finds

$$a = \frac{\Delta\nu}{Z_i(l+\frac{1}{2})}\frac{l(l+1)}{j(j+1)}\cdot\frac{g(I)}{1838}\text{ cm}^{-1}. \qquad (4)$$

Earlier applications of these formulas gave unsatisfactory results, the nuclear magnetic moment calculated from the hyperfine structure of different levels of the same atom gave entirely different values. The discrepancy could be explained only in part by the approximate nature of the formulas. Since then it has been shown by

[1] For this formula and the others compare Pauling and Goudsmit, *Structure of Line Spectra*, page 209, reference 1 and page 60.

Breit[2] and by Racah[3] that large relativity corrections must be made to the above formulas. For non-s states a corrected equation (4) was used, which indeed seemed to remove the discrepancy between the values of the nuclear magnetic moment obtained from the two levels of the same doublet. For s states one did *not* use a corrected equation (2) but used numerically calculated approximate eigenfunctions because the factor in Eq. (2) is proportional to $\psi(0)^2$, the square of the value of the eigenfunction at the origin. The calculations showed that there remained a large discrepancy between the values of the magnetic moment obtained from an s state and from other states.

It is a remarkable fact that this discrepancy is much decreased if one uses Eq. (2) with relativity corrections instead of the approximate values of $\psi(0)^2$. Already McLennan, McLay and Crawford[4] had shown that Eq. (2) is well in agreement with their observations on the hyperfine structure in the spectra of thallium. Furthermore Professor Breit[5] informed me that the value of $\psi(0)^2$ for the 6s state of Cs calculated by Nile by means of a more accurate method than the one used in previous applications comes out to be in very good agreement with Eq. (2). We are thus inclined to believe that the following equations (solved for $g(I)$) are suitable to give fair approximations for the nuclear magnetic moment.

For s electrons:

$$g(I)=\frac{3a}{8R\alpha^2}\frac{n_o^3}{Z_iZ_o^2}\frac{1838}{\kappa(\frac{1}{2},Z_i)}, \tag{5}$$

for non-s electrons:

$$g(I)=\frac{aZ_i}{\Delta\nu}\frac{j(j+1)(l+\frac{1}{2})}{l(l+1)}\frac{\lambda(l,Z_i)}{\kappa(j,Z_i)}1838. \tag{6}$$

In these expressions $\kappa(j, Z_i)$ is the relativity correction by which Eq. (2) for the hyperfine structure has to be multiplied, $\lambda(l, Z_i)$ is the same for the multiplet separation Eq. (3). These corrections are given by Eqs. (7) and (8). Table I contains these quantities for $j=\frac{1}{2}$ and $1\frac{1}{2}$ and for $l=1$, for various Z_i values.[3, 6]

$$\kappa(j,Z_i)=4j(j+\tfrac{1}{2})(j+1)/(4\rho^2-1)\rho,\quad \rho^2=(j+\tfrac{1}{2})^2-(\alpha Z_i)^2, \tag{7}$$

$$\lambda(l,Z_i)=[2l(l+1)/(\alpha Z_i)^2]\{[(l+\tfrac{1}{2})^2-(\alpha Z_i)^2]^{\frac{1}{2}}-1-[l^2-(\alpha Z_i)^2]^{\frac{1}{2}}\}. \tag{8}$$

In the application of the above formulas the following remarks are of practical importance. In many-electron spectra the same electron causes often part or all of the hyperfine splitting of several levels. Expressions are known[7] to obtain the value of a for this electron from the various hyperfine structures. If these values turn out to be consistent with each other it may not be considered as a support for the formulas given in the present paper. Only when the values of $g(I)$ calculated from different electrons of the same atom agree can one take this as supporting the validity of the approximations involved.

In a one-electron spectrum the choice of the quantities n_o, Z_o and Z_i is well defined. For s-electrons it will be correct to put $Z_i=Z$, the actual nuclear charge, as the contribution to the interactions comes mainly from the region near the nucleus. For p-electrons Z_i as obtained from the doublet formula (3) is throughout the periodic table about equal to $(Z-4)$. It is not

TABLE I.

Z_i	κ $j=\frac{1}{2}$	κ $j=1\frac{1}{2}$	λ $l=1$
10	1.01	1.00	1.00
20	1.04	1.01	1.00
30	1.09	1.02	1.01
40	1.18	1.03	1.03
50	1.30	1.05	1.05
60	1.49	1.07	1.08
70	1.78	1.10	1.12
80	2.25	1.15	1.17
85	2.61	1.17	1.20
90	3.10	1.20	1.24
92	3.36	1.21	1.27

[2] Breit, Phys. Rev. **38**, 463 (1931).

[3] Racah, Zeits. f. Physik **71**, 431 (1931).

[4] McLennan, McLay and Crawford, Proc. Roy. Soc. **A133**, 652 (1931).

[5] Breit, Phys. Rev. **42**, 348 (1932).

[6] Back-Landé, *Zeemaneffekt und Multiplettstruktur*, page 96.

TABLE II.* *Nuclear magnetic moments and g-values.*

Z	Element	Atomic weight	I	Magnetic moment	$g(I)$	Remarks
3	Li	7	$1\frac{1}{2}$	3.29	2.19	
13	Al	27	$\frac{1}{2}$	2.1	4.2 B	
29	Cu	63	$1\frac{1}{2}$	2.5	1.7 B	
		65	$1\frac{1}{2}$	2.5	1.7	
31	Ga	69	$1\frac{1}{2}$	2.01	1.34 A	$g(71)/g(69)=1.27$
		71	$1\frac{1}{2}$	2.55	1.70	
33	As	75	$1\frac{1}{2}$	0.9	0.6 C	
37	Rb	85	$2\frac{1}{2}$	1.3	0.5 C	Rb87 perhaps $I=2\frac{1}{2}$, magnetic moment 3.0, $g(I)=1.2$
		87	$1\frac{1}{2}$	2.7	1.8	
48	Cd	111	$\frac{1}{2}$	−0.67	−1.33 B	It is not certain whether 111, 113 or both cause the observed hyperfine structure
		113	$\frac{1}{2}$	−0.67	−1.33	
49	In	115	$4\frac{1}{2}$	5.4	1.2 B	
51	Sb	121	$2\frac{1}{2}$	2.7	1.1 B	$g(121)/g(123)=1.80$
		123	$3\frac{1}{2}$	2.1	0.6	
80	Hg	199	$\frac{1}{2}$	0.55	1.1 B	$g(199)/g(201)=-2.70$
		201	$1\frac{1}{2}$	−0.62	−0.41	
81	Tl	203	$\frac{1}{2}$	1.8	3.6 A	$g(205)$ about 1% or 2% larger than $g(203)$
		205	$\frac{1}{2}$	1.8	3.6	
82	Pb	207	$\frac{1}{2}$	0.60	1.20 A	
83	Bi	209	$4\frac{1}{2}$	4.0	0.89 A	

* References: Li: reference 9.
Al: Ritschl, Nature **31**, 58 (1933).
Cu: Ritschl, Zeits. f. Physik **79**, 1 (1932).
Ga: Campbell, Nature, in print.
As: Tolansky, Proc. Roy. Soc. **A137**, 541 (1932).
Rb: Kopfermann, Naturwiss. **21**, 24 (1933).
Cd: see Bacher and Goudsmit, *Atomic Energy States.*
In: Jackson, Zeits. f. Physik **80**, 59 (1933).
Sb: Badami, Zeits. f. Physik **79**, 206 and 224 (1932).
Hg, Tl, Pb, Bi, see Bacher and Goudsmit, *Atomic Energy States.*

true that this is the same Z_i as the one occurring in the hyperfine structure formula, the former is the average fourth power, the latter the average third power of the effective nuclear charge. One thus expects for the hyperfine structure Z_i to be somewhat smaller than $(Z-4)$, but how much smaller is quite uncertain. For heavy elements this uncertainty will be within the limit of accuracy of the method employed, but for lighter elements and also for larger l-values, d- and f-orbits, the error will become appreciable, causing the calculated $g(I)$ to be too small.

For a many-electron configuration one must first apply the formulas given in the above-mentioned papers[6, 7] to derive the a-values for the individual electrons. For non-s electrons similar formulas exist[8] which give the $\Delta\nu$ separations for the individual electrons, for p^2 and p^4 for instance, one has to use the total ^3P separation. In the case of p^3, where the multiplet separations are zero in first order, all one can do is to take the ^3P separation of the next ion and decrease it slightly to allow for the screening by the third p-electron.

When a single inner s-electron occurs in several configurations it is found that its a-value is practically the same for all of them. This means that there is hardly any screening effect caused by the other electrons. If there is a slight change the largest value of a should be the one where one expects the screening to be least and one may consider this a-value as the one the s-electron has

[7] Goudsmit and Bacher, Phys. Rev. **34**, 1501 (1929); Goudsmit, Phys. Rev. **37**, 663 (1931).

[8] Goudsmit, Phys. Rev. **31**, 946 (1928); Humphreys and Goudsmit, Phys. Rev. **31**, 960 (1928); Pauling and Goudsmit, reference 1, p. 157.

in that stage of ionization of the atom in which it is the only outer electron. One should use in Eq. (5) the Z_o and n_o for that particular ion. For instance if one obtains a for the $5s$ electron from the hyperfine structure of the $5s$ $8s$ level in neutral cadmium one must use Eq. (5) for once ionized cadmium with this a-value.

More complicated configurations cannot be used in general, unless one is able to obtain some detailed information from the multiplet structure about the coupling scheme of the various angular momentum vectors. The results obtained will not be very reliable.

Table II contains the nuclear magnetic moments and g-values for elements for which the hyperfine structure allows the application of the method described in this paper. The value for lithium is not obtained by this method, but taken from the very accurate calculations made by Breit and Doermann.[9] All other results should be considered as preliminary only. In the table the results have been graded A, B, C to denote whether they have been obtained from a few independent hyperfine separations or not. Because of the lack of sufficient data for several elements some personal judgment is needed when Eqs. (5) and (6) have to be applied to a more complicated electron configuration. I consider it therefore better not to discuss in detail the derivations of the results given in Table II, but rather wait for more extensive data to eliminate as much as possible the subjective factor.

[9] Breit and Doermann, Phys. Rev. **36**, 1732 (1930); Granath, Phys. Rev. **42**, 44 (1932).

Paschen-Back Effect of Hyperfine Structure and Polarization of Resonance Radiation. Cadmium ($6^1P_1-5^1S_0$)

N. P. HEYDENBURG, *Department of Physics, State University of Iowa*

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Because of the Paschen-Back effect of the hyperfine structure of the odd isotopes, the polarization of cadmium λ2288A resonance radiation excited by plane polarized incident light changes from 76.7 percent in zero field to 100 percent in a strong field parallel to the electric vector of the exciting light. The experimental results agree very closely with computations based on Goudsmit's modification of Darwin's theory of the Paschen-Back effect and give for the separation of the two levels into which the 6^1P_1 level of Cd (odd-isotopes) is split a value of 12.6×10^{-3} cm^{-1}. From this result and Schüler's measurements of the hyperfine separations of the triplet lines $6^3P_{0,1,2}-6^3S_1$ the constants a and b giving the interactions of the p and s electrons, respectively, from Goudsmit's equation

$$A(J)=a(2-g)-a\frac{6\Gamma(2-g)-2(g-1)L(L+1)}{(2L-1)(2L+3)}+b(g-1)$$

are found to be $a=8.4\times10^{-3}$ and $b=225.7\times10^{-3}$.

THE polarization of the cadmium resonance lines λλ2288A and 3261A has been discussed by Ellett and Larrick[1] on the basis of Schüler's[2,3] explanation for the hyperfine splitting of the Cd energy levels. It will be recalled that Schüler has assigned nuclear moments of 0 and $\frac{1}{2}$ (in units $h/2\pi$) to the even and odd isotopes of Cd, respectively. For the λ2288A line, using nonpolarized exciting light, Ellett and Larrick found for the polarization in zero field

$$P=(3+9\gamma)/(11+9\gamma)100,$$

where γ is the ratio of the abundance of the even and odd isotopes which they found from experimental data to have the value 2.53. From observations of Schrammen[4] and the narrowness of the Cd red line λ6438.47A ($7^1D_2-6^1P_1$), it is known that the line λ2288A is very narrow therefore the splitting of the upper level caused by the interaction of the nucleus with the valence electrons must be small. Hence it is reasonable to suppose that a Paschen-Back effect should occur for these levels in rather small fields.

Up to the present time the components of the λ2288A line have not been resolved by spectroscopic methods. However measurements of the polarization for different fields should lead to information on the separation of these components, for it will be shown later that the theoretical equation of the polarization as a function of the field strength depends on a parameter β which determines the separation of the hyperfine levels. In order to derive the expression for the polarization as a function of the field strength it is necessary to obtain the various Zeeman transition probabilities as functions of the field. As the Zeeman pattern of the λ2288A line for the even isotopes with $I=0$ is a normal pattern excitation with either perpendicular or parallel components alone will give complete polarization for all field strengths. Therefore these components need no further consideration. The Zeeman pattern for the odd isotopes with $I=\frac{1}{2}$ given in Fig. 1 is similar to that of the sodium D lines. Darwin[5] and also Heisenberg and Jordan[6] have published theoretical discussions of the Zeeman effect in intermediate fields for ordinary multiplets. The latter authors have worked out the explicit intensity formulas for the sodium D type doublets. However, these formulas must be altered somewhat for our case as we are dealing with the interaction of the nuclear spin and the angular momentum of the valence electrons so that different

[1] Ellett and Larrick, Phys. Rev. **39**, 294 (1932).
[2] Schüler and Brück, Zeits. f. Physik **56**, 291 (1929).
[3] Schüler and Keyston, Zeits. f. Physik **67**, 433 (1931).
[4] Schrammen, Ann. d. Physik **83**, 1161 (1927).
[5] Darwin, Proc. Roy. Soc. **A115**, 1 (1927).
[6] Heisenberg and Jordan. Zeits. f. Physik **37**, 263 (1926).

g values will be involved. Goudsmit[7] has pointed out that we can use the formulas derived for ordinary multiplets by Darwin after replacing m_s and m_l by $g_i m_i$ and $g_j m_j$, respectively. After making these changes and associating with a given Zeeman level the quantum numbers m_i and m_j appropriate to strong fields we find the intensities to be given by the following formulas:

$$
\begin{aligned}
|z'|^2(1, \tfrac{1}{2}, -\tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) &= 2\{1+[\beta-\omega(g-g_i)]/\Delta_-\},\\
|z'|^2(1, -\tfrac{1}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) &= 2\{1+[\beta+\omega(g-g_i)]/\Delta_+\},\\
|z'|^2(1, \tfrac{1}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) &= 2\{1-[\beta-\omega(g-g_i)]/\Delta_-\},\\
|z'|^2(1, -\tfrac{1}{2}, \tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) &= 2\{1-[\beta+\omega(g-g_i)]/\Delta_+\},\\
|x'-iy'|^2(1, \tfrac{3}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) &= 2,\\
|x'-iy'|^2(1, \tfrac{1}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) &= \{1-[\beta-\omega(g-g_i)]/\Delta_-\},\\
|x'+iy'|^2(1, -\tfrac{1}{2}, -\tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) &= \{1-[\beta+\omega(g-g_i)]/\Delta_+\},\\
|x'+iy'|^2(1, -\tfrac{3}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) &= 2,\\
|x'-iy'|^2(1, \tfrac{1}{2}, \tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) &= \{1+[\beta-\omega(g-g_i)]/\Delta_-\},\\
|x'+iy'|^2(1, -\tfrac{1}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) &= \{1+[\beta+\omega(g-g_i)]/\Delta_+\},
\end{aligned}
$$

where $\Delta_-=\{(\beta-\omega(g-g_i))^2+8\beta^2\}^{\frac{1}{2}}$; $\Delta_+=\{(\beta+\omega(g-g_i))^2+8\beta^2\}^{\frac{1}{2}}$

and β is the separation constant of the hyperfine levels. The brackets on the left give the quantum numbers of the upper and lower levels involved in the transitions in the order (f, m_f, m_i; f', m_f', m_i').

In calculating the polarization of the resonance radiation two additional factors must be taken into consideration, the intensity distribution in the source and the separation of the hyperfine levels in zero field. In order to obtain an approximate value of the separation of these levels the polarization will first be calculated for a source with uniform intensity distribution across the absorption region. It seems reasonable to suppose that this will give nearly correct values of the polarization as the source was operated at a fairly high temperature but very low Cd vapor pressure insuring a broad line free from self-reversal. The polarization is then obtained by the usual method of finding the population in resonance of the upper levels, then the intensity in resonance of each component, the polarization being given by $P=(I_\perp-I_{||})/(I_\perp+I_{||})$, where $I_\perp$ and $I_{||}$ are the sums of the intensities of all the perpendicular and parallel components, respectively. Completing these computations we find for the case where the incident light is plane polarized with its electric vector parallel to the field H

$$P_{||}=\frac{16x^4+32x^2+27}{16x^4+48x^2+63}100, \qquad (1)$$

where $x=g\omega/2\beta=gehH/8\pi mc\beta$. In plotting $P_{||}$ against H we obtain a family of curves, a curve for each value of the parameter β.

The value of β, giving that curve which most

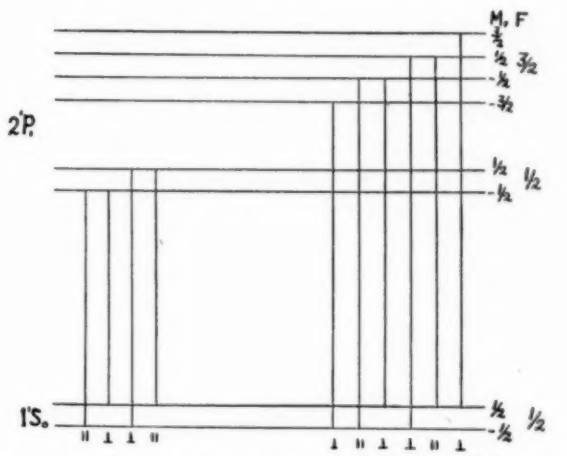

FIG. 1. Zeeman pattern for the odd isotopes with $I=\frac{1}{2}$.

[7] Pauling and Goudsmit, *Structure of Line Spectra*, p. 219

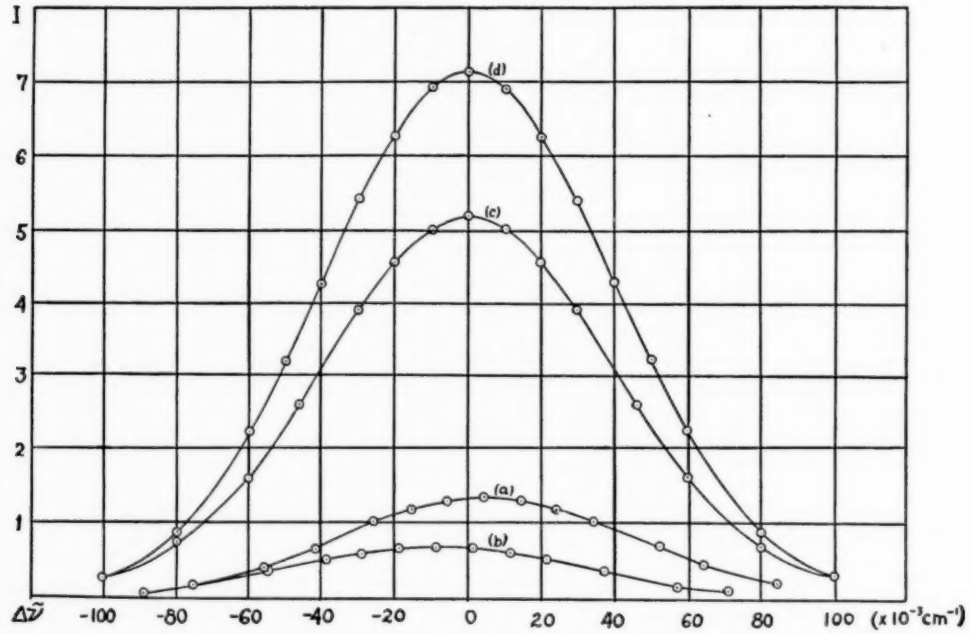

FIG. 2. Intensity curves for the three components in the source.

nearly coincides with the experimental curve, can then be used in calculating the polarization when the theoretical distribution of intensity in the source is taken into account. This intensity distribution can be computed from the known formula for the Doppler broadening of spectral lines,

$$I = I_0(c/\nu_0) \exp\left[-a^2c^2(\nu/\nu_0 - 1)^2\right], \qquad (2)$$

where $a^2 = M/2RT$, M being the molecular weight, R the molecular gas constant and c the velocity of light. In Fig. 2 are plotted the intensity curves of the three components in the source taking its temperature to be 727°C. Curve (c) is the component due to the even isotopes. Curves (a) and (b) represent the two hyperfine components of the odd isotopes when the value of β is taken to be 4.2×10^{-3} cm^{-1} which was obtained by comparing the theoretical curves using Eq. (1) and the experimental curve of $P_{||}$ against H (Fig. 5). These add to give the resultant curve (d). As this curve has very nearly the same half value breadth as curve (c) it may be represented without appreciable error by Eq. (2) without changing the value of the temperature. Thus the energy radiated from the source at a given frequency range ν to $\nu+d\nu$ is given by

$$dI = I_1(c/\nu_1) \exp\left[-a_1^2c^2(\nu/\nu_1 - 1)^2\right]d\nu. \qquad (3)$$

The energy absorbed in the resonance bulb by a component of frequency ν_2 for this same frequency range is

$$dI' = \{I_2(c/\nu_2) \exp\left[-a_2^2c^2(\nu/\nu_2 - 1)^2\right]\}$$
$$\{I_1(c/\nu_1) \exp\left[-a_1^2c^2(\nu/\nu_1 - 1)^2\right]\}d\nu. \qquad (4)$$

Integrating this value over all frequencies we obtain for the total energy absorbed

$$I' = \frac{B}{\nu_1\nu_2} \exp\left[-\frac{a_1^2a_2^2c^2(\nu_2-\nu_1)^2}{a_1^2\nu_2^2 - a_2^2\nu_1^2}\right], \qquad (5)$$

where B is a constant depending upon the relative intensity of the absorbing line. The frequency shift of the Zeeman components with changing field strengths is readily obtained from the equations for the energy of the Zeeman levels. The relative population in resonance of the upper levels can be calculated from Eq. (5), then the polarization is obtained as before.

After comparing the curve obtained by plotting these new values of the polarization against the field strength with the experimental curve, it may be necessary to change the value of the separation constant β to give better agreement. This

new value assigned to β must then be used to recalculate the polarization. Hence it is seen that by a series of approximations we may approach very closely the theoretical polarization based on the theoretical intensity distribution in the source.

Experimental

The experimental set-up was the same as that described by Ellett and Larrick.[1] A monochromator was used to eliminate the λ3261A resonance line. The vapor pressure of Cd in the source was maintained sufficiently low so that the red line of Cd was faint compared to the hydrogen $H\alpha$ line. Under these conditions no appreciable self-reversal of the λ2288A line should have occurred. The resonance bulb was operated at temperatures between 100° and 105°C well below the temperature at which depolarization due to secondary radiation occurs. A calibrated Helmholtz coil wound with copper tubing through which water flowed for cooling was used to obtain the magnetic field at the resonance bulb, its axis being parallel to the direction of the incident beam.

Polarization measurements were made photographically by the Cornu method with Wollaston prisms as in the work of Olson.[8] In this method one of the Wollastons is rotated about their common axis until two of the images on the photographic plate are of equal intensity. The polarization is then given by the cosine of twice the angle of rotation measured from the position of the fixed prism. In the actual determination of this angle three or four photographs were taken at various angles within the region of the probable match position. A microphotometer curve of the cross section of each image was taken. The area under these curves as measured by a planimeter was taken to be a measure of the intensity of the image. This is justified in the present case as the images compared were nearly of the same intensity and were exposed and developed together. The function $x=(C-D)/(C+D)$, where C and D are the intensities of the two images on a plate, was then plotted against the angle made by the Wollaston prism. Fig. 3 shows a typical curve obtained in this manner. The angle at which the line crosses the axis is taken as the angle where the two images would have exactly the same intensity.

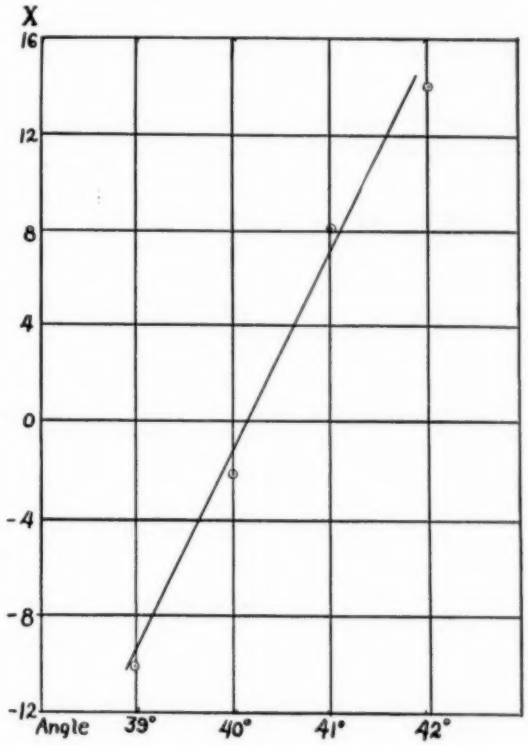

Fig. 3.

For the Cd line λ2288A an exposure time of $2\frac{1}{2}$ to 3 hours was necessary to obtain photographs of sufficient intensity for measuring purposes hence after the general outline of the experimental curve of polarization against field strength was obtained, the other points were found by estimating the angle at which the images should be matched, then a photograph was taken at a small angle either side of this position and the actual match position determined from these. All of the points on the experimental curve with the exception of one were obtained before the form of the theoretical curve had been determined. Several photographs were taken throughout the course of the experimental work with the heat removed from the resonance bulb and as no images could be detected on these films it was certain that stray light had been eliminated.

It is necessary to correct the experimental values of the polarization for the depolarization caused by the slight convergence of the incident beam after passing through the lens system. The

[8] Olson, Phys. Rev. **32**, 443 (1928).

depolarization due to the divergence of the beam which passed through the Wollaston prisms is negligible as the angle of maximum divergence of the rays was less than 3°. Gaviola[9] discussed this depolarization effect for the case of plane polarized incident light. A similar correction for the case of nonpolarized light is easily calculated. Fig. 4 illustrates how the incident intensity is

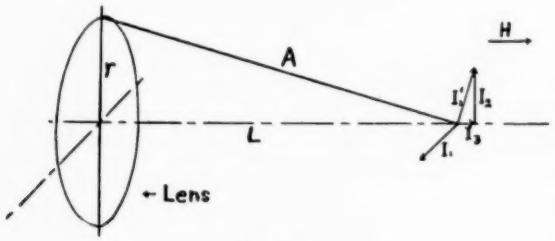

FIG. 4.

split up into components parallel and perpendicular to the field. The intensity of a ray A may be represented by two mutually perpendicular equal components I_1 and I_1' one of which is chosen perpendicular to the field H. The other can then be split into components I_2 perpendicular to the field and I_3 parallel to the field. Integrating over the aperture of the lens we obtain for the intensity of the perpendicular component

$$I_\perp = \int^{\text{over lens}} (I_1+I_2)ds = I_0\pi \int_0^R \left(\frac{r^2+2L^2}{r^2+L^2}\right) r dr$$

and for the parallel component

$$I_{||} = \int^{\text{over lens}} I_3 ds = I_0\pi \int_0^R \frac{r^3 dr}{r^2+L^2},$$

where I_0 is the intensity of the radiation passing through a unit area of the lens. When the aperture is small compared to the focal length of the lens, I_0 may be considered as constant over the lens aperture. The amount of depolarization resulting from the presence of the parallel component can be readily calculated for each field strength by determining the difference between the theoretical value of the polarization with and without this added parallel component. For zero field this correction becomes

$$Y = \left\{\frac{3+9\gamma}{11+9\gamma} - \frac{105(2-x)}{274-8x}\right\},$$

where $x = R^2/L^2$ while for very large fields it reduces to

$$Y = 4x/(4+x).$$

The value of x for the experimental set-up used was 0.010.

DISCUSSION

Obviously we cannot compare the measured polarization values directly with those given by Eq. (1) as the measurements are for the case of excitation by perpendicular components and are the resultant polarizations from components of both even and odd isotopes. It can easily be proved that the polarization $P_\perp$ of the components from the odd isotopes alone in terms of the polarization P_0 of the components from both even and odd isotopes is given by the following formula

$$P_\perp = (3\gamma - 3\gamma P_0 - 4P_0)/(-\gamma+\gamma P_0 - 4). \quad (6)$$

Then from the equation

$$P_{||} = 2P_\perp/(1-P_\perp) \quad (7)$$

relating the polarization $P_\perp$ for excitation with perpendicular components to the polarization $P_{||}$ for excitation with parallel components we obtain values which can be compared with those given by Eq. (1).

In the first four columns of Table I are given respectively, the experimental values as measured, the values corrected for the depolarization caused by the convergence of the incident beam, the values $P_\perp$ obtained from Eq. (6), and the values $P_{||}$ obtained from Eq. (7). It will be noticed that the experimental value P_0 for zero

TABLE I. *Experimental values of the polarization for different magnetic fields.*

P observed	P_0 corrected	$P_\perp$ odd isotopes	$P_{||}$ odd isotopes	H (gauss)
76.3%	76.7%	27.3%	42.7%	0
76.8	77.3	28.8	44.7	75
79.3	79.9	36.0	53.0	144
81.9	82.5	43.4	60.5	200
85.5	86.2	54.4	70.5	255
88.3	89.1	63.4	77.6	315
91.3	92.1	73.0	83.7	375
94.0	95.0	82.6	90.5	563

[9] Gaviola and P. Pringsheim, Zeits. f. Physik **34**, 1 (1925).

field differs slightly from that obtained previously by Ellett and Larrick,[1] their value not having been corrected for the convergence of the incident beam. This gives 2.6 as the value of the constant γ instead of 2.53.

In Table II are recorded the theoretical values of the polarization for different field strengths.

TABLE II. *Theoretical values of the polarization as a function of field strength.*

P_{II} (calc. from 1)	P_{II} (calc.)	H (gauss)
42.7%	42.7%	0
48.6	48.9	100
54.5	54.8	150
62.0	62.4	200
69.1	69.6	250
75.0	75.6	300
79.8	80.5	350
83.3	84.0	400
88.8	89.2	500
91.8	92.1	600

In the first column are the values computed from Eq. (1) by using $\beta=4.2\times10^{-3}$ cm^{-1}, and in the second column are the values obtained on taking into account the theoretical intensity distribution in the source. These differ very little from those in the first column.

In Fig. 5 the theoretical values of the polarization calculated from Eq. (1) are plotted against the field H and compared with the extrapolated experimental values givin in column 4 of Table I. Fig. 6 gives a comparison of the theoretical curve by using the values of the polarization given in column 2 of Table II with the experimental curve. As the general agreement of the curves in Fig. 6 has not changed appreciably from that in Fig. 5 it may be said that the consideration of the intensity distribution in the source has not effected a noticeable correction to the value of β previously assigned.

Fig. 7 gives a comparison of the experimental curve with two theoretical curves having values of β relatively 10 percent larger and smaller than that in Fig. 6. These curves lie outside the range of experimental error hence we may safely say that the value $\beta=4.2\times10^{-3}$ cm^{-1} is correct to within 10 percent error. The separation of the two hyperfine levels of the odd isotopes is then $3\beta=12.6\times10^{-3}$ cm^{-1}. The accuracy of this determination represents a resolving power of 3.5×10^{7}. As a resolving power of this magnitude is not available by use of present spectroscopic methods this is the only means of determining the separation of these levels at present.

In order to resolve spectroscopically the hyperfine components of the line λ6438.47A ($7'D_2-6'P_1$) resulting from the separation of the $6'P_1$ level a resolving power of 1.2×10^{6} would be required if the components had zero breadth. Since the line breadth cannot be entirely eliminated and the much stronger component due to the even isotopes is superimposed on the hyperfine pattern, it is not feasible at present to detect any variation from the intensity distribution given by a single line.

Goudsmit[10] has derived the following equation for the hyperfine splitting constant A, where A is just twice the constant β used above,

$$A(J)=a(2-g)-a\frac{6\Gamma(2-g)-2(g-1)L(L+1)}{(2L-1)(2L+3)}+b(g-1) \quad (8)$$

as usual $\Gamma=[J(J+1)-L(L+1)-S(S+1)]/2$, while a and b determine the absolute value of the splitting due to the p and s electrons, respectively. The A's for the triplet levels $^3P_{1,2}$, $^3S_1$ and the singlet level $^1P_1$ have been calculated using Eq. (8) giving

$$A(^3P_1)=3a/2+b/2, \quad =148.6\times10^{-3}\text{ cm}^{-1}, \quad (9)$$

$$A(^3P_2)=3a/10+b/2, \quad =120.0\times10^{-3}\text{ cm}^{-1}, \quad (10)$$

$$A(^3S_1)=b, \quad =264.0\times10^{-3}\text{ cm}^{-1}, \quad (11)$$

$$A(^1P_1)=a, \quad =8.4\times10^{-3}\text{ cm}^{-1}. \quad (12)$$

The numerical values given for the triplet levels were obtained from Schüler's data[2,3] on the separation of the hyperfine components of the triplet lines $6^3P_{0,1,2}-6^3S_1$ (λλ4678, 4800, 5086A). The value of $A(^1P_1)$ is that found by the author. Schüler's results provide a unique solution as well as a check for the values of a and b. It will be noticed however that his results are not sufficiently accurate for a determination of the smaller constant a, for if the value of b from Eq. (11) is substituted into Eqs. (9) and (10) positive and negative values for a are obtained respectively.

[10] Goudsmit, Phys. Rev. **37**, 663 (1931).

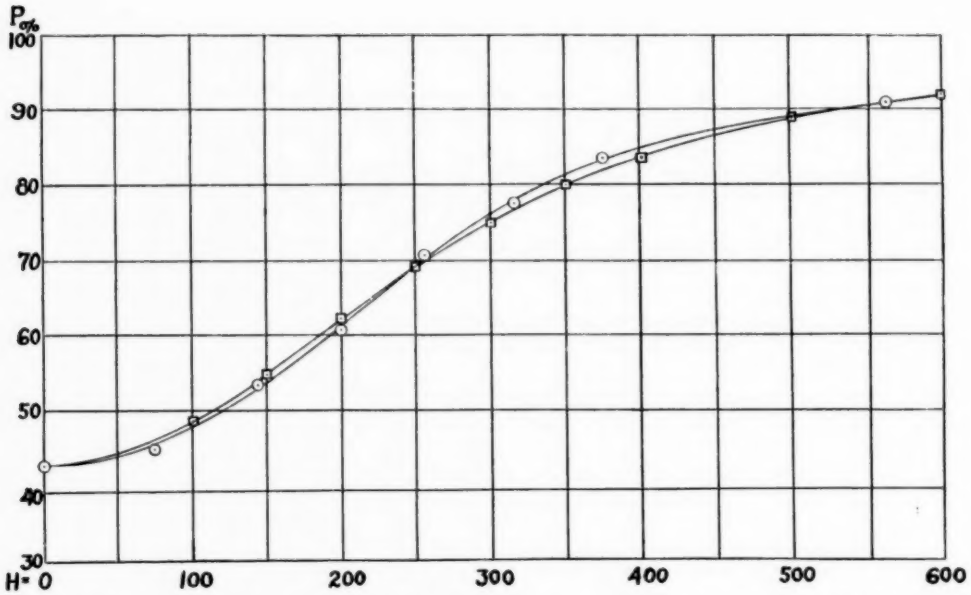

FIG. 5. Theoretical values of polarization from Eq. (1) and experimental values (column 4, Table I) plotted against magnetic field. Circle with dot, experimental curve; square with dot, theoretical curve. $\beta = 4.2 \times 10^{-3}$ cm^{-1}.

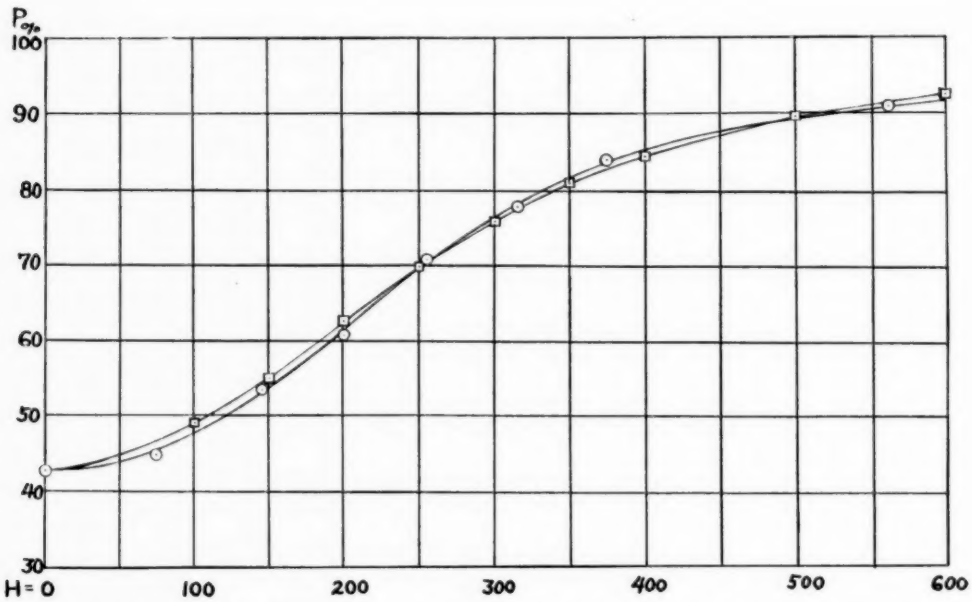

FIG. 6. Plot of theoretical values of polarization (column 2, Table II) with the experimental values. Circle with dot, experimental curve; square with dot, theoretical curve.

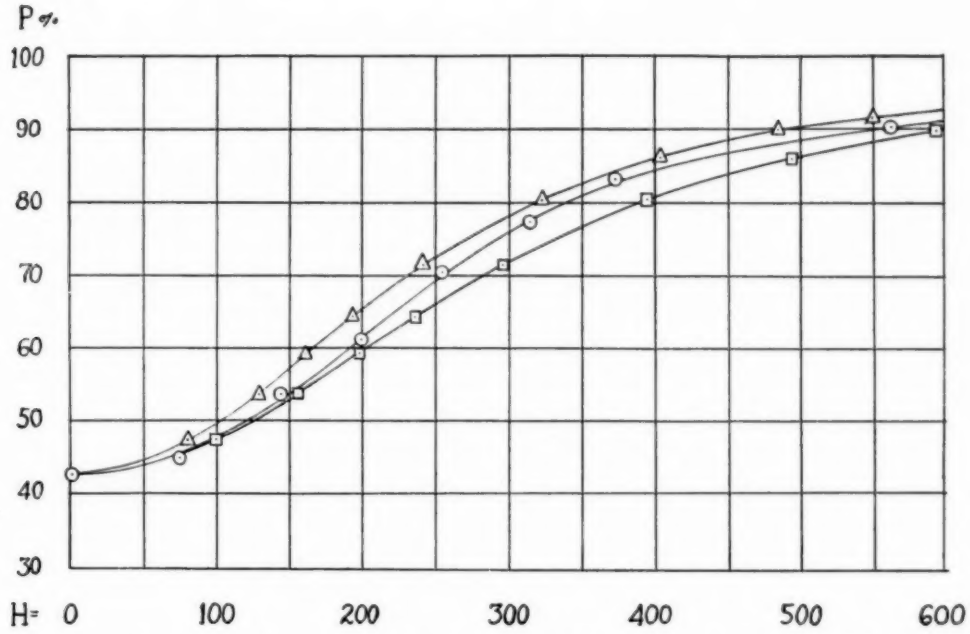

FIG. 7. Comparison of experimental curve for polarization with two theoretical curves. Circle with dot, experimental curve; square with dot, $A=9.25\times10^{-3}$ cm^{-1}; triangle with dot, $A=7.57\times10^{-3}$ cm^{-1}.

If we substitute the mean value of b from Schüler's results and the value from a of Eq. (12) into Eqs. (9) and (10) we obtain

$$A(^3P_1)=135.0\times10^{-3}\text{ cm}^{-1},$$
$$A(^3P_2)=124.9\times10^{-3}\text{ cm}^{-1}.$$

As these values differ by less than 10 percent from those obtained directly from Schüler's results they are probably within the range of his experimental error.

In conclusion I wish to express my thanks to Dr. Ellett for his many helpful suggestions throughout the progress of the work.

Notes on the Stark Effect

E. U. CONDON, *Princeton University*

(Received March 1, 1933)

The theory of the Stark effect in atomic spectra is discussed in general terms and it is shown that large effects arise when two terms which are related to each other in such a way as to satisfy the optical combining rules come close together in the spectrum. Fairly good values of the Stark displacements in complicated atoms may be obtained simply by using the hydrogenic values of the matrix components involved in the theoretical formulas. The ideas are illustrated by discussion of the existing data on the spectra of nickel, lithium, carbon spark, and argon.

THERE exists in the literature of spectroscopy a large amount of experimental data referring to the Stark effect in atomic spectra which has not been hitherto brought into any kind of relation to the modern theory of atomic structure. Of course the effect, and its theoretical interpretation, for atomic hydrogen is very well known and has played an important rôle in development of the theory. Likewise the work of Foster[1] and of Dewey[2] on the effect in helium has brought the theory into satisfactory relation with experiment there. Some work has also been done on the small quadratic effect on the resonance lines of sodium and potassium, but in addition to these contributions a glance for example at the Stark effect chapter in the *Handbuch der Experimental Physik* (Volume 21) will show a considerable amount of uncorrelated experimental data. In this paper the aim is to show how the theory may be used to throw light on some of this material and to point the way for further work in this field.

§1. Theory of the Stark Effect

If H_0 is the Hamiltonian of the unperturbed atom and if $\mathbf{P}$ is the electric moment of the atom and $\mathbf{E}$ the applied electric field, then the Hamiltonian for the atom in the field is

$$H = H_0 - \mathbf{E}\cdot\mathbf{P}. \tag{1}$$

The alteration of energy levels and proper states is therefore governed, in accordance with usual theory, by the matrix components of $\mathbf{P}$. Moreover the only component of $\mathbf{P}$ that is effective is that along $\mathbf{E}$ so we may choose axes so this is the z-component. Now P_z is the same quantity which governs that part of the dipole radiation of atoms which is polarized with its electric vector parallel to the z-axis. Therefore the selection rules and other calculations of its matrix components which have been made for the theory of line intensities are applicable here. Writing $(A|P|B)$ for the matrix component of P_z which connects two unperturbed energy states A and B we know that $(A|P|B)$ vanishes unless:

(a) A and B are of opposite parity (Laporte rule), (b) $J_B = J_A$ or $J_A \pm 1$ where J_B and J_A are the resultant angular momentum quantum numbers of B and A respectively,

(c) $M_{JA} = M_{JB}$ where M_{JA} and M_{JB} are the z-components of resultant angular momentum of the atom in the two states measured with $h/2\pi$ as unit.

These three properties are rigorous. In addition, insofar as it is accurate to assign electronic configuration labels to the terms we may say:

(d) Configuration A may differ from configuration B at most in regard to one electronic n, l value.

Likewise in case of Russell-Saunders coupling in which resultant spin angular momentum S and resultant orbital angular momentum L are quite accurately diagonal when H_0 is diagonal we may say that $(A|P|B)$ vanishes unless

(e) $S_A = S_B$.

(f) $L_B = L_A$, $L_A \pm 1$.

In addition for Russell-Saunders coupling the actual dependence on L, S, J and M_J is the same

[1] Foster, Proc. Roy. Soc. **A114**, 47 (1927) and **A117**, 137 (1927).

[2] Dewey, Phys. Rev. **28**, 1108 (1926) and **30**, 770 (1927).

as that which in the intensity theory leads to the well-known Kronig-Russell-Hönl formulas.

So far as orders of magnitudes are concerned we may expect that the nonvanishing components will be of the same order as if calculated with hydrogen-like eigenfunctions for the individual electrons of the atom. For this reason we note that Schrödinger's calculations for hydrogen give

$$(n, l-1, m|EP|n, l, m) = -\frac{3}{2} eEna_0 \left[\frac{(n^2-l^2)(l^2-m^2)}{4l^2-1}\right]^{\frac{1}{2}} \quad (2)$$

for the matrix component connecting two states of equal n value and of l value differing by unity. Here a_0 is the first Bohr radius. Expressing energy in cm^{-1} and taking 100 kv/cm as the unit of E the coefficient of the irrational expression in (2) becomes

$$6.43n \quad cm^{-1} \text{ per } 100 \text{ kv/cm}.$$

The maximum value assumed by the radical for fixed n and varying l and m is about $n/3^{\frac{1}{2}}$ so far n not greater than 10 the matrix component is under 200 cm^{-1} in value in all cases for fields up to 100 kv/cm. This field is about the largest which has been used in ordinary Stark effect investigations.

Suppose now we put such a perturbing term into the Hamiltonian of an atom and consider what may be said in general about the result. The perturbed states will become linear combinations of such of the unperturbed states as are joined by nonvanishing matrix components of the perturbation. Therefore quantities which were quantum numbers in the unperturbed problem lose their significance after the perturbation. Thus it is no longer possible to speak of a state as being definitely odd or even, also the J value loses its precision, but M_J retains its status as an accurate quantum number.

The extent to which this tendency is realized the perturbation theory shows to be related to the nearness of the unperturbed terms. If W_A and W_B are the unperturbed energies of states A and B and $(A|EP|B)$ is the perturbation component connecting them then the perturbed states will be appreciable linear combinations of A and B if $(A|EP|B)$ is comparable with or large compared to $(W_A - W_B)$. If $(A|EP|B) \ll (W_A - W_B)$ then the alteration in the perturbed states is relatively small as is also the change in energy. In this case so far as the change in energy is concerned due simply to the matrix component connecting A and B it is such as to displace the upper state upward and the lower state downward each by the same amount, namely.

$$|(A|EP|B)|^2/|W_A - W_B|. \quad (3)$$

The states A and B thus seem to "repel" each other.

As to the amount of this "repulsion" of two terms it is generally rather small. For weaker fields a common value of $(A|EP|B)$ would be 15 cm^{-1} whereas the terms (A and B) may be separated by 1000 cm^{-1} so the perturbation of each would amount to 0.22 cm^{-1}. The small quadratic Stark effect of any state A is the sum of the actions of this type of all other states B of the atom which have matrix components connecting it with A. Most of the theoretical work on the Stark effect of alkalis, like that of Unsöld[3] and of Kirkwood,[4] is concerned with attempts to sum up, for particular states A, like the normal state, or the first resonance state, the whole effect of all other states which perturb it.

But such effects are never comparable with the relatively large effect in atomic hydrogen. Nevertheless such large Stark effects are observed in other atomic spectra. Large Stark shifts may occur in other atoms if two terms connected by a matrix component $(A|EP|B)$ are closer together in the unperturbed energy scheme than the energy value $(A|EP|B)$. In particular if A and B have zero interval in the unperturbed scheme then they will give rise to two levels in the perturbed scheme, one of which is moved up by $(A|EP|B)$ and the other down by the same amount. This makes it clear why large Stark effect displacements are relatively rare in spectra other than hydrogen. The matrix components $(A|EP|B)$ are rather severely restricted by the selection rules. Even when nonvanishing they are quite small so that it is something of an exceptional case when two states A and B which are connected by the perturbation matrix are close

[3] Unsöld, Ann. d. Physik **82**, 355 (1927).

[4] Kirkwood, Phys. Zeits. **33**, 521 (1932).

together relative to the magnitude of $(A|EP|B)$.

The condition for large Stark effect just set out is more general than the one given by Bohr[5] before the new quantum mechanics which is usually used by experimental workers in qualitative discussions of their data. Bohr pointed out that we may expect large effects for a spectral term that is nearly hydrogen-like, i.e., one which if equated to Rh/n^{*2} leads to a nearly integral value of n^*. This was regarded as indicating that the electronic orbit was effectively in a Coulomb field and hence the hydrogen-like behavior was to be expected. But it did not give a means of estimating the magnitude of the effect. The account of the theory we have given shows clearly the justification of Bohr's rule. If a particular term is almost hydrogen-like then we may be fairly sure that terms arising from an electron configuration in which one of the electronic l values is increased by unity will also be hydrogen-like. If both are nearly hydrogen-like terms they will be near each other and so produce a large effect. The essential thing is nearness of W_A and W_B for nonvanishing $(A|EP|B)$ and Bohr's rule gives us a convenient way of noticing what is in point of fact a large class of the cases in which large Stark effects are observed. The rule is sufficient though not necessary so we may expect to find cases in which the effect is large even though the perturbed states are not hydrogen-like in their energy values.

The rule was enunciated before the development of Pauli's principle with its sound basis for getting true n values. In those days if n^* was nearly an integer it was thought that the nearest integer was the true value of n. Now we know that n^*-n may become as great as several units so that a term may be apparently hydrogen-like through having (n^*-n) be almost exactly equal to an integer instead of zero. This is in fact the case in silver, where there is a good-sized Stark effect that comes about from the nearness of the $6d^2D$ to the $4f^2F$, both being very close to the hydrogenic value for $n=4$.

In what follows attention will be paid to the application of the perturbation theory to the discussion of the existing data for the spectra of several elements. The general standpoint will be that the effect has to be calculated by finding the allowed values of $H_0-\mathbf{E}\cdot\mathbf{P}$ which can be done in view of the smallness of the matrix components of $\mathbf{E}\cdot\mathbf{P}$ by solving the finite secular equation which represents the interaction of just those interacting terms which are within a few hundred wave numbers of each other on the energy scale.

§2. Nickel

To illustrate how the principles of the preceding section may be used to throw some light on the experimental data, even in a case that is too complicated for detailed discussion at present, let us consider the Stark effect in nickel. The only observations apparently are those of Takamine,[6] which were made a decade before the analysis of the spectrum by Russell.[7] Of the fifty lines for which Takamine records Stark displacements, twenty-nine may be found in Russell's list of classified lines. These are all transitions from levels of the high even configurations d^8s5s, $d^9 4d$, $d^9 6s$, $d^9 5d$ and $d^8 s4d$ to the intermediate odd configurations $d^9 4p$ and $d^8 s4p$. The final states have term values between 25,000 and 33,000 cm^{-1} above the normal state. As there are no even configurations in this region we conclude that the Stark displacement of these terms is very small.

The initial states involved in the identified lines fall into two groups, one between 49,000 and 51,000 cm^{-1}, and the other between 54,000 and 57,000 cm^{-1}. Taking the ionization limit to be 61,579 cm^{-1} we find that the hydrogenic terms are 49,400 cm^{-1} for $n=3$ and 54,730 cm^{-1} for $n=4$. For the lower group the configurations are $(3d)^9 4d$ and $(3d)^4 4s5s$, so these are not $n=3$ states for valence electrons. But these lower even configurations occupy the same region in the energy diagram as does the odd $d^9 5p$ which is known from Russell's analysis. So it is more in accord with our general principles to regard the Stark effect as an interaction of $d^9 4d$ and $d^8 s5s$ with $d^9 5p$ which is induced by the applied field and to regard the nearness to a hydrogenic value as accidental. Similarly the upper group of even terms is in the correct position to interact with $d^9 6p$ but as this configuration has not been identi-

[5] Bohr, Proc. Phys. Soc. London **35**, 275 (1923) and Ann. d. Physik **71**, 228 (1923).

[6] Takamine, Astrophys. J. **50**, 1 (1919).

[7] Russell, Phys. Rev. **34**, 821 (1929).

fied in the spectrum as yet we must confine our attention to the lower group of initial states.

This further restriction reduces the number of identified lines for which Takamine gives Stark displacements to twelve, listed in Table I. The first column gives Takamine's wave-length, the second that of the identified line in Russell's paper which I take to be the same line (there is a systematic difference of about 0.2A). The third column gives the identification in terms of Russell's multiplet analysis, the fourth and fifth are the shifts in wave numbers of the parallel and perpendicular polarized components as observed by Takamine for the values of the field strength given in the sixth column of the table. The line 5142.77 is given two alternative identifications by Russell both of which are listed in the table.

It will be noticed that e^3F_4 occurs as initial state for the first, second, fifth and eleventh lines in the table. The nearness of the equality of their Stark displacements, when these are reduced to the same field strength assuming a variation with E^2, is an indication of the accuracy to which the whole effect may be attributed to the upper state. In the twelve lines there are eight different initial

TABLE I. *Stark effect in nickel I.*

(Takamine)	(Russell)	Identification	$\Delta\nu$ (cm^{-1}) $\parallel$	$\perp$	Field (kv/cm)
4410.66	4410.50	$z^5D_3^0-e^3F_4$	+6.1	+4.1	39
4937.45	4937.33	$z^5F_4^0-e^3F_4$	+5.0	+5.5	38.5
5018.48	5018.30	$z^3D_1^0-e^3F_2$	−2.8	0.0	38.5
5082.55	5082.38	$z^3P_1^0-e^3P_1$	−1.7	−0.97	38.5
5084.20	5084.07	$z^3D_3^0-e^3F_4$	+5.0	+5.4	38.5
5142.91	5142.77	$z^3D_2^0-f^3D_2$ $z^5F_2^0-f^3D_3$	+0.34	+0.26	21.8
5146.61	5146.48	$z^3D_2^0-e^3F_4$	+0.44	+0.26	21.8
5155.90	5155.76	$z^1D_2^0-e^1F_3$	+3.0	+3.0	21.8
5176.72	5176.56	$z^1D_2^0-f^1D_2$	+0.56	+0.34	21.8
5184.78	5184.59	$z^3D_2^0-e^3P_1$	−1.1	−1.1	21.8
5462.69	5462.48	$z^1F_3^0-e^3F_4$	+2.9	+1.9	21.8
5588.09	5587.85	$a^3P_2-y^3D_2^0$	+0.48	+0.35	21.8

states represented. All the terms show a displacement upward in energy except e^3P_1 and e^3F_2. According to the ideas of §1 we therefore expect that the nearest odd combining term to each of these terms will be below the perturbed term, except for these two for which the nearest combining term is above. This is in fact the case as Table II shows. In Table II are listed in the successive columns: the name of the term, its configuration, the name and configuration of the

TABLE II.

Perturbed term	Configuration	Nearest perturbing term	Interval (cm^{-1})
e^3F_4	d^94d	$3D_3^0d^95p$	−5.2
e^3F_2	d^94d	$3D_1^0d^95p$	+16.7
e^1F_3	d^94d	$^3F_4^0d^85p$	−42.5
e^3P_1	d^94d	$^3D_2^0d^95p$	+12.0
e^5F_4	d^8s5s	$6^0J=3$	−53.3
f^3D_2	d^94d	$^3D_3^0d^95p$	−0.5
f^3D_3	d^94d	$^3D_2^0d^95p$ $^3D_3^0d^95p$	−86.5 +56.1
f^1D_2	d^94d	$^1D_2^0d^95p$	−65.0
$y^3D_2^0$	d^8s4p	$^3D_2d^95s$	−15.11

nearest term which could perturb it, and the interval between the perturbed term and this nearest term in cm^{-1} counted negative if the perturbing term is below the perturbed term and positive if it is above. Of course the designations perturbed term and perturbing term are simply relative to the particular lines under discussion; actually the perturbation is mutual and (if it existed) Stark effect data on lines involving the terms called "perturbing" here should show that they are perturbed by amounts equal and opposite to their perturbing action on the terms here called "perturbed."

The table shows that we should expect f^3D_2 to show a strong upward perturbation whereas f^3D_3 would probably show a very small perturbation since the nearest terms are relatively far from it and there are two, one above and one below of roughly the same distance whose effects tend to cancel. Since the Stark effect for 5142.77 is actually quite small this tells us unambiguously that this line is to be identified with the second of the two alternatives offered by Russell's analysis. It is believed that this is the first time that a doubtful point in an analysis of a complex spectrum has been settled by reference to the expected Stark effect of the lines.

In the absence of more complete experimental data it is not thought worthwhile to attempt more precise discussion of the relations involved in the theory. It is felt, however, that even these rough agreements suffice to show that the Takamine data are in accord with the general outlines of the theory of the Stark effect.

§3. LITHIUM

The experimental data for lithium are summarized in the *Handbuch der Experimental*

Physik (Volume 21) article by Stark, page 479. All of it refers to combinations in which $2s$ or $2p$ are the final states. Either of these should have extremely small effects owing to their great separation from the nearest terms of opposite parity. Therefore we expect the line shifts to be essentially those of the corresponding upper states. Evidence for this is found in comparing the recorded shifts of $2s$–$5p$ and $2p$–$5p$, assuming these to be quadratic effects. The former is -5.5 cm^{-1} at 0.26 unit (1 unit $=10^5$ volt/cm) while the latter is -45.5 cm^{-1} at 0.8 unit. Writing $\Delta\nu = kE^2$ corresponding values of k are 81. and 72. respectively.

In this spectrum the doublet separations are negligibly small. Also the excited states are fairly hydrogen-like. Let us first consider the effect of the field on the states with $n=4$. The unperturbed energy values relative to the $4d$ term are:

$4s$	-1611.7 cm^{-1}	$4d$	0.0
$4p$	$-\ 154.7$	$4f$	$+7.4$

The matrix components of electric interaction we may expect to be close to the values given by (2) for hydrogen. In any case the relative magnitudes will be given quite accurately by (2) and this is all that matters for a description of the pattern. We may expect a fairly strong interaction between $4d$ and $4f$, a smaller effect on $4p$ and a quite small effect on $4s$. The secular equation for $m=3$ is linear and tells us that this substate of the $4f$ term is not affected by the field. Owing to the selection rule on m this does not show up in combinations with $2p$. For $m=2$ it is a quadratic equation connecting these substates of $4d$ and $4f$. Using the matrix components for (2) and the empirical $4d$–$4f$ separation we find the roots to be

$$\lambda = 3.7 \pm [3.7^2 + 25.8^2 E^2]^{\frac{1}{2}}$$

when measured from the $4d$ level.

Likewise for $m=1$ the secular equation is a cubic connecting corresponding substates of the $4p$, $4d$ and $4f$ terms:

$$\begin{vmatrix} -154.7-\lambda & -39.8E & 0 \\ -\ 39.8E & -\lambda & -32.5E \\ 0 & -32.5E & 7.4-\lambda \end{vmatrix} = 0.$$

For $m=0$ the secular equation is a quartic but here the $4s$ term is so far away compared to the size of the perturbation that its effect may be neglected. The matrix component connecting $4s$ and $4p$ has the value 56.9 for unit field strength so the perturbation due to interaction of these terms is $(56.9)^2/1457.0 = 2.2$ cm^{-1} which is negligible compared to the main effect. Even the $4p$–$4d$ interaction is quite small so that all of the secular equations may with good accuracy be taken simply as quadratics connecting the $4d$ and $4f$ levels. If we do this we obtain as the levels

$$\lambda_2 = 3.7 \pm [(3.7)^2 + 25.8^2 E^2]^{\frac{1}{2}}$$
$$\lambda_1 = 3.7 \pm [(3.7)^2 + 32.5^2 E^2]^{\frac{1}{2}}$$
$$\lambda_0 = 3.7 \pm [(3.7)^2 + 34.5^2 E^2]^{\frac{1}{2}}.$$

In Fig. 1 these levels are plotted against E. The experimental points are from the date of Snyder[8] on λ4602 which is the combination with $2p$. The agreement is quite good. This calculation makes no reference to the doublet character of the spectrum and so is not in accord with Snyder's suggestion concerning the line's behavior.[9]

Similar remarks may be made concerning the group of levels for $n=5$. In combination with $2p$ only the substates with $m=0$, 1 and 2 are effec-

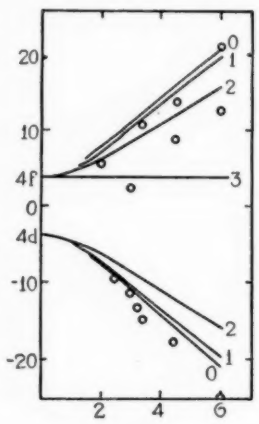

FIG. 1.

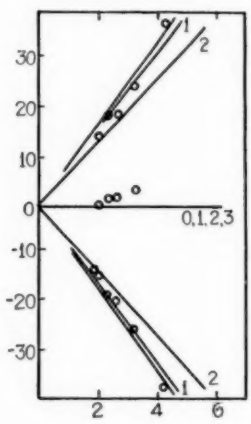

FIG. 2.

FIG. 1. Stark displacements due to interaction of $4d$ and $4f$ terms in lithium. Ordinates, displacement in cm^{-1}; abscissas, field strength in 10^4 volt/cm. The points are observed displacements of the lines $4d-2p$ and $4f-2p$.

FIG. 2. Stark displacements due to interaction of $5d$, $5f$ and $5g$ terms in lithium. Ordinates, displacement in cm^{-1}; abscissas, field strength in 10^4 volt/cm. The points are observed displacements of the combinations with the $2p$ term.

[8] Snyder, Phys. Rev. **33**, 354 (1929).

[9] Reference 8, bottom of page 359.

tive. The energies relative to $5d$ are:

$5s$	-798.2	$5f$	$+7.8$
$5p$	$-\ 84.0$	$5g$	$7.8<?<10$
$5d$	0.0		

where probable limits for the unknown $5g$ are merely suggested. In the field the perturbed eigenstates become linear combinations of the almost coincident $5d$, $5f$, $5g$ terms. The $5p$ is not so far away but that its displacement is appreciable. With the second-order perturbation formula this term must be pushed up by $5s$ and down by $5d$ giving as its displacement in unit field -57 cm^{-1} which is in fair agreement with the values -81 and -72 obtained experimentally. The displacement of the line $2p$–$5s$ corresponds to a downward displacement in unit field of the $5s$ term of 28 cm^{-1}. The theoretical value is 12. cm^{-1}.

The group $2p-(5d+5f+5g)$ may be discussed easily by omitting the $5p$ interaction and neglecting the small and empirically uncertain intervals between these initial state terms. Doing this the energy levels are given by

$$\lambda_2=\pm 64.2E, \quad \lambda_1=\pm 77.5E, \quad \lambda_0=\pm 81.4E.$$

In Fig. 2 the data of Snyder are plotted together with the straight lines given by the theory.

Similarly the line $2p$–$6s$ shows a shift corresponding to a displacement of $6s$ of -32 cm^{-1} in unit field whereas the theoretical push from $6p$ is -45 cm^{-1}. The displacement of the $6p$ term in unit field as inferred from the $2p$–$6p$ line is -163 cm^{-1}. The theoretical value is the difference between the upward push from $6s$ and the downward push of $6d$ which comes out to be -200 cm^{-1}. Since the experimental data are rough and the theoretical values depend on the square of matrix components which are taken from hydrogen it is felt that the agreement here presented is good enough to indicate that the ideas of §1 are adequate for a discussion of the main effect.

§4. Carbon Spark

The data are some observations made by Ishida and Fukushima[10] and are believed to be the only data on a nonhydrogenic ion spectrum. The displacements, as is to be expected, correspond to smaller values of the matrix components than in arc spectra. The matrix components are in fact roughly half the hydrogenic values which is the factor of reduction to be expected for orbits in a Coulomb field with $Z=2$.

Their Fig. 2a gives the results of observation on λ2747.31 and λ2746.50 which is the transition, $s^2 3p^2P-s^2 4d^2D$, in CII. The shift is to longer wave-lengths and corresponds to $k=-0.004$ in the equation $\Delta\nu=kE^2$ where $\Delta\nu$ is in cm^{-1} and E is in 10^4 volt/cm. Likewise their Fig. 2b gives the data on λ4267.27 and λ4267.02 which is $s^2 3d-s^2 4f$. Here the k is about $+0.002$ in the same units. Attributing these shifts to the upper states we see that they are due to the interaction of the $s^2 4d$ term and the $s^2 4f$ term. The $4d$ term is 855 cm^{-1} below the $4f$ term and so the $4d$ term is pushed down in energy and the $4f$ term is pushed up, which is in accord with the facts.

An interesting feature of their Fig. 2b is the fact that there is an unshifted component in the $\perp$ polarization which is absent in the $\parallel$ polarization. This is due to the fact that the $m=3$ substates in ^2F are unperturbed since there is no $m=3$ substate in ^2D to perturb them. In combining with ^2D to form a radiative transition the $m=3$ substate of ^2F must jump into an $m=2$ substate of ^2D which accounts for the presence of the unshifted component in the $\perp$ but not in the $\parallel$ polarization.

The hydrogenic matrix component for $m=0$ connecting the $4d$ and $4f$ states for a field of 10^4 volt/cm is 3.44 cm^{-1} from Eq. (2). The value of the matrix component corresponding to empirical k of 0.002 and $\Delta\nu$ of 855 is 1.37 cm^{-1} or roughly half of the hydrogenic value. This is largely due to the fact that we are dealing with an ion rather than a neutral atom, also to the fact that the pictures are blends of components for $m=1$ and $m=2$ for which the matrix components are smaller.

Their data on λ2992.63 furnish an excellent example of the interaction of terms as sketched in §1. This is the transition $s^2 3d-s^2 5f$. The experimental value of k is -0.018. At first sight this appears to be an exception to our general rules as the field makes it go down in energy and yet the $5d$ term, below it, should push it up.

[10] Ishida and Fukushima, Sci. Papers Inst. Phys. Chem. Research **14**, 123 (1930).

This is due to the presence of a $5g$ term. This term is not known experimentally but we will not be far wrong if we place it at the exact hydrogenic value for $n=5$. The $5f$ term is 144 cm^{-1} lower than this and the $5d$ is 462 cm^{-1} lower than $5f$. Assuming hydrogen-like matrix components (divided by 2 because we have an ion) and these empirical term separations we calculate for k the value

$$k=-(2.43)^2/144+(3.45)^2/462=-0.015.$$

Here the first term is the downward push due to $5g$ and the second the upward push due to $5d$; the final value is in good agreement with the experimental, -0.018.

These are all the data on this spectrum which are available. Theory agrees with experiment as accurately as could be expected and, in particular, explains the difference in the behavior of the $4f$ and $5f$ terms.

§5. Argon

The effect in argon has been investigated recently by Ryde.[11] He measured the displacements of a large number of lines and has given in his Table VII the displacement of the energy levels produced by a field of 100 kv/cm. The configuration $p^5 5d$ is given with some completeness and his Fig. 3 shows how the displacement of a term is greater the smaller its difference from the hydrogenic value for $n=5$. In argon the states may be separated into two sets, one built on the state $p^5\,{}^2P_{\frac{1}{2}}$ of the ion, the other on $p^5\,{}^2P_{\frac{3}{2}}$ of the ion. Combinations between the two sets are weak.

Looking at the data from the viewpoint of this paper, we see that the $p^5 5d(^2P_{\frac{1}{2}})$ terms are perturbed downward because of a repulsion from the $p^5 5f(^2P_{\frac{1}{2}})$ terms which lie in a close group at just the hydrogenic value reckoned down from $^2P_{\frac{1}{2}}$ of A II. Hence distance from hydrogenic value is here synonymous with distance from nearest perturbing term. At present we do not have very good knowledge of the coupling relations in argon so it is hard to give a detailed discussion of the interaction of the $5d$ with the $5f$ terms. Neglecting the separation between the $5f$ terms, the perturbation of any particular $5d$ term due to the $5f$ terms is

$$\Delta\nu=\sum_{\beta}\frac{|(5d_\alpha|E\cdot P|5f_\beta)|^2}{(W_{5d}{}^\alpha-W_{5f}{}^\beta)},$$

where the sum extends over all the $5f$ terms in the group. If the numerator is about the same for all the d terms the $\Delta\nu$ values should lie on a hyperbola whose axis is the location of the $5f$ group, i.e., about 4400 cm^{-1}. Using the hydrogenic value with $m=0$ of the $5d$–$5f$ interaction from Eq. (2) for the numerator we have 5770. In Fig. 3 is plotted the

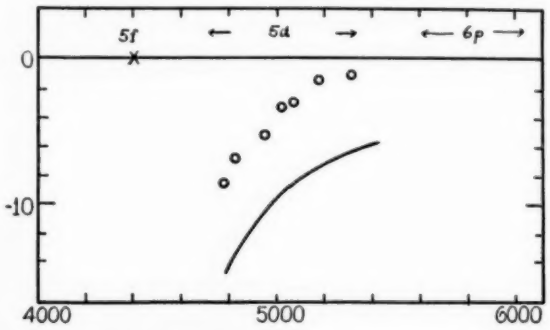

Fig. 3. Stark displacements of the several $p^5 5d(^2P_{3/2})$ terms in argon, showing relation of the displacement to nearness to the perturbing $p^5 5f$ and $p^5 6p$ groups of terms. Ordinates, displacement in energy in field of 10^5 volt/cm; abscissas, term values of the terms in cm^{-1}. The hyperbola is drawn, using hydrogenic values of the matrix component connecting $5d$ and $5f$.

curve $(5770)/(W_{5d}-W_{5f})$ together with points showing Ryde's experimental values for the corresponding term displacements in a field of 100 kv/cm. It is seen that the observed values agree with this curve in order of magnitude but drop to zero more rapidly than does the hyperbola representing interaction with $5f$. This might be due to a variation of the numerator with the $5d$, but another cause which is certainly acting is the upward push on the $5d$ terms from the $6p$ group which is not so very far below the $5d$ terms.

[11] Ryde, Zeits. f. Physik **77**, 516 (1932).

On the Magnetization of Ferromagnetic Crystals

FRANCIS BITTER, *Westinghouse Research Laboratories*

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In a previous article a function E_θ is discussed. This function gives the energy of a crystal as a function of the direction of magnetization. The present paper contains photographs of plaster models representing E_θ for an undistorted crystal of nickel, for an undistorted crystal of iron in zero applied field, and in a field of 100 oersteds parallel to the [100], [110], and [111] axes respectively, and for an iron crystal distorted by compression and extension along the above mentioned axes. Assuming that a crystal is magnetized to saturation in the direction in which E_θ has a minimum, magnetization curves for crystals distorted as mentioned above are calculated and illustrated.

IN a previous article[1] a procedure was outlined for describing some properties of strained ferromagnetic crystals. It is proposed to discuss the consequences of this procedure in greater detail. In the following pages certain aspects of magnetization are taken up.

PROCEDURE

Let i, j, k be subscripts denoting measurement along three axes parallel to the tetragonal axes of a cubic ferromagnetic crystal whose spontaneous magnetization is I_w. The orientation of I_w is given by the direction cosines $\alpha_i, \alpha_j, \alpha_k$. The crystal may be distorted and the distortion described by the components of a strain tensor, A_{ij}. The energy for an arbitrary direction of magnetization is assumed to be:—

$$E_\theta = c\sum{}'\alpha_i^2\alpha_j^2 + K_1\sum A_{ii}\alpha_i^2 + K_2\sum{}'A_{ij}\alpha_i\alpha_j - I_w\sum\alpha_i H_i + \text{const.} \quad (1)$$

From this expression it is possible to calculate the magnetostriction in an arbitrary direction β_i, β_j, β_k.

$$\delta l/l = \chi_0 + \chi_1\sum\alpha_i^2\beta_i^2 + \chi^2\sum{}'\alpha_i\alpha_j\beta_i\beta_j. \quad (2)$$

The constants involved in Eq. (2) are related to those in Eq. (1).

$$\chi_1 = -K_1/(c_{11}-c_{12}); \quad \chi_2 = -K_2/2c_{44}. \quad (3)$$

The quantities c_{11}, c_{12}, c_{44} are the elastic constants of the cubic crystal under discussion. It is further assumed that the actual direction of magnetization of the crystal for any given set of external conditions is that direction in which E_θ has a minimum. If E_θ has minima in two or more directions ambiguities may arise.

EVALUATION OF CONSTANTS

For nickel[2] the constant c is approximately -2.5×10^4 ergs/cc and $I_w = 500$. For iron all the constants may be evaluated with sufficient accuracy to give some idea of the predictions of Eq. (1). From observations by Honda and Masiyama[3] we can evaluate χ_0, χ_1, and χ_2, as has been done in a previous article.[1] Certain constants, s_{11}, etc., related to the above elastic constants, c_{11}, etc., by the following equations:

$$c_{11} = s_{11}+s_{12}/(s_{11}+2s_{12})(s_{11}-s_{12}),$$
$$c_{12} = -s_{12}/(s_{11}+2s_{12})(s_{11}-s_{12}),$$
$$c_{44} = 1/s_{44},$$

were measured for iron by Goens and Schmid.[4] From their measurements we obtain $c_{11} = 0.237\times10^{13}$; $c_{12} = 0.141\times10^{13}$; and $c_{44} = 0.116\times10^{13}$ ergs/cc. Knowing the magnetostriction and the elastic constants, we may with the help of Eq. (3) evaluate K_1 and K_2. The constant c for iron is taken from Akulov.[5] The values of the various constants of Eq. (1) for iron as used in this paper

[1] F. Bitter, Phys. Rev. **42**, 697 (1932).

[2] F. Bitter, Phys. Rev. **38**, 546 (1931).

[3] K. Honda and Y. Masiyama, Sci. Rep. Tohoku Univ. **15**, 755 (1926).

[4] E. Goens and E. Schmid, Naturwiss. **19**, 520 (1931).

[5] N. Akulov, Zeits. f. Physik **57**, 249 (1929); **67**, 794 (1931).

are: $c=2.15\times10^5$; $K_1=-3.06\times10^7$; $K_2=2.85\times10^7$ ergs/cc; $I_w=1718$.

The Representation of E_θ

It is difficult to visualize the properties of the function E_θ without a rather wearisome lot of computing. Since E_θ promises to be of importance in the study of ferromagnetism, and perhaps also in the study of certain non-ferromagnetic crystals,[6] I have thought it worth the trouble to make a few models for representative values of the parameters involved. Various methods of representation are, of course, possible. Spherical polar coordinates were chosen. Thus, since E_θ defines an energy for any direction, we may represent E_θ by a surface surrounding a certain point in such a way that the length of the radius vector to the surface in any given direction is equal to E_θ for that direction. The disadvantage of this representation is that negative radii are not desirable. The arbitrary constant in Eq. (1) is therefore so chosen that the figure has a reasonable size and does not become negative. In other words, the length of the radius of the model is not proportional to the corresponding energy, but the difference in length between any two radii is proportional to the difference between the two corresponding energies.

The particular conditions illustrated below were chosen in such a way as to cover the most important aspects of the problem. The intention is to show what shapes the function E_θ may assume rather than to carry out the calculations for cases of experimental importance. This is especially apparent below when we speak of elastic compressions of 50 percent, etc., which are, of course, not experimentally realizable.

The first term in Eq. (1) contains only one parameter c, giving rise to two different types of material, one, like iron, for which $c>0$, and another, like nickel, for which $c<0$. The remaining terms in Eq. (1) represent the influence of crystal distortion and of an externally applied magnetic field. We shall consider these last terms only for a crystal of iron, and only for the six special cases listed in Table I.

It is to be observed that we have chosen distortions which give rise to no volume change.

Table I. *The parameters used in the illustrations of E_θ. H is the magnetic field, and e is the elongation.*

$H \parallel [100]$ $H_i=H$; $H_j=H_k=0$
$H \parallel [110]$ $H_i=H_j=H/2^{\frac{1}{2}}$; $H_k=0$
$H \parallel [111]$ $H_i=H_j=H_k=H/3^{\frac{1}{2}}$
$e \parallel [100]$ $A_{ii}=e$; $A_{jj}=A_{kk}=-e/2$; $A_{ij}=A_{jk}=\cdots=0$
$e \parallel [110]$ $A_{ii}=A_{jj}=e/4$; $A_{kk}=-e/2$; $A_{ij}=A_{ji}=3e/4$; $A_{jk}=\cdots=0$
$e \parallel [111]$ $A_{ii}=A_{jj}=A_{kk}=0$; $A_{ij}=A_{ji}=A_{jk}=\cdots=e/2$

These distortions are not produced by the application of ordinary tension or compression. On the other hand the results obtained will be very similar to those resulting from true tension and compression, and in addition are particularly simple to calculate.

The Function E_θ

Figs. 1 and 2 represent the function E_θ for the special case $A_{ii}=A_{ij}=\cdots=0$, $H=0$, i.e., for the undisturbed ideal lattice. Since the constant c for nickel is not only negative, but also ten times smaller than for iron, Fig. 1, if constructed on the same scale as Fig. 2, would not deviate much from sphericity. The scale used for Fig. 1 is such that 1 cm represents 1718/500 times as many ergs as a like distance in Fig. 2. Since the ratio 1718/500 is that of the saturation intensities, the scale chosen is such that a field H produces the same effect on the model for iron as on the model for nickel. In all the photographs here reproduced the plaster model stands next to a crystal model. In every case the axes of adjacent models are parallel. From Fig. 1 we see that in nickel E_θ has maxima in the direction of the tetragonal [100] axes, and minima in the direction of the trigonal [111] axes, whereas in iron, as shown in Fig. 2, the maxima and minima are reversed. In Figs. 3, 4, and 5 we have E_θ for iron in a field of 100 oersteds parallel to the [100], [110], and [111] axes respectively. In Figs. 6, 7, 8 and 9 are illustrated the effect of compression and elongation on E_θ in the absence of a magnetic field. Figs. 8 and 9 are two views of the same set of figures. Referring to Table I, compression corresponds to $e<0$, elongation corresponds to $e>0$. In the photographs the model on the left represents $e>0$, or elongation and the model on the right $e<0$, or compression. The stick resting on the crystal model in the center of each illustration

[6] F. Bitter, Phys. Rev. **42**, 731 (1932).

FIG. 1. E_θ for an undistorted nickel crystal.

FIG. 2. E_θ for an undistorted iron crystal.

FIG. 3. E_θ for an iron crystal in a field of 100 oersteds parallel to a [100] axis.

FIG. 4. E_θ for an iron crystal in a field of 100 oersteds parallel to a [110] axis.

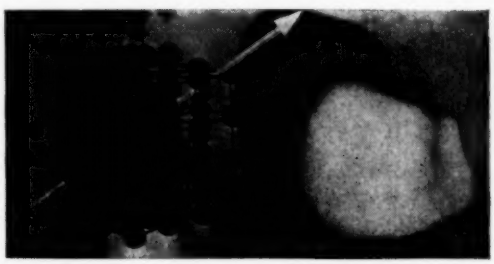

FIG. 5. E_θ for an iron crystal in a field of 100 oersteds parallel to a [111] axis.

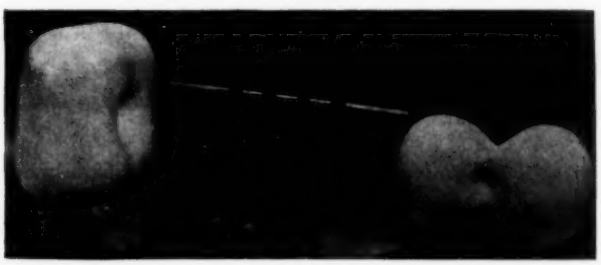

FIG. 6. On the left, E_θ for an iron crystal elastically stretched 1 percent along a [100] axis. On the right, E_θ for an iron crystal elastically compressed 1 percent along a [100] axis.

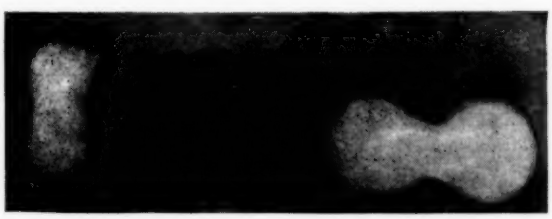

FIG. 7. On the left, E_θ for an iron crystal elastically stretched 1 percent along a [110] axis. On the right, E_θ for an iron crystal elastically compressed 1 percent along a [110] axis.

FIG. 8. On the left, E_θ for an iron crystal elastically stretched 1 percent along a [111] axis. On the right, E_θ for an iron crystal elastically compressed 1 percent along a [111] axis.

FIG. 9. A second view of the models shown in Fig. 8.

represents the direction of elongation or contraction. The models were all made for $e=\pm 0.01$. All the models in Figs. 2–9 are made on precisely the same scale except the model on the left of Fig. 6. For this model a slightly larger additive constant was used to avoid negative values of E_θ. The models in Fig. 6 depend only on c and K_1, while those in Figs. 8 and 9 depend only on c and K_2, as may readily be verified by substituting the values listed in Table I into Eq. (1). Because K_1 and K_2 in iron have opposite signs compression along a [100] axis has an effect on E_θ similar to extension along a [111] axis. Further, as has already been pointed out,[1] E_θ for compression along a digonal [110] axis depends on K_2, K_1+K_2, and K_1-K_2.

MAGNETIZATION

The magnetization curves obtained by applying a field parallel to the elongation or compression in Figs. 6, 7, 8 and 9 are shown in Figs. 10, 11 and 12. The cross-hatched portions of the curves indicate that there is a transition from one minimum of E_θ to another, and that we therefore have a transition in some unspecified manner from one magnetization curve to another. Some of the magnetization curves are vertical for $H=0$. These vertical portions also involve transitions from one minimum of E_θ to another. Experimental evidence already presented[5] indicates that for $e=0$, the curves as drawn represent the behavior of actual iron crystals fairly well. As far as I know, no experimental data exist with which to check the other curves.

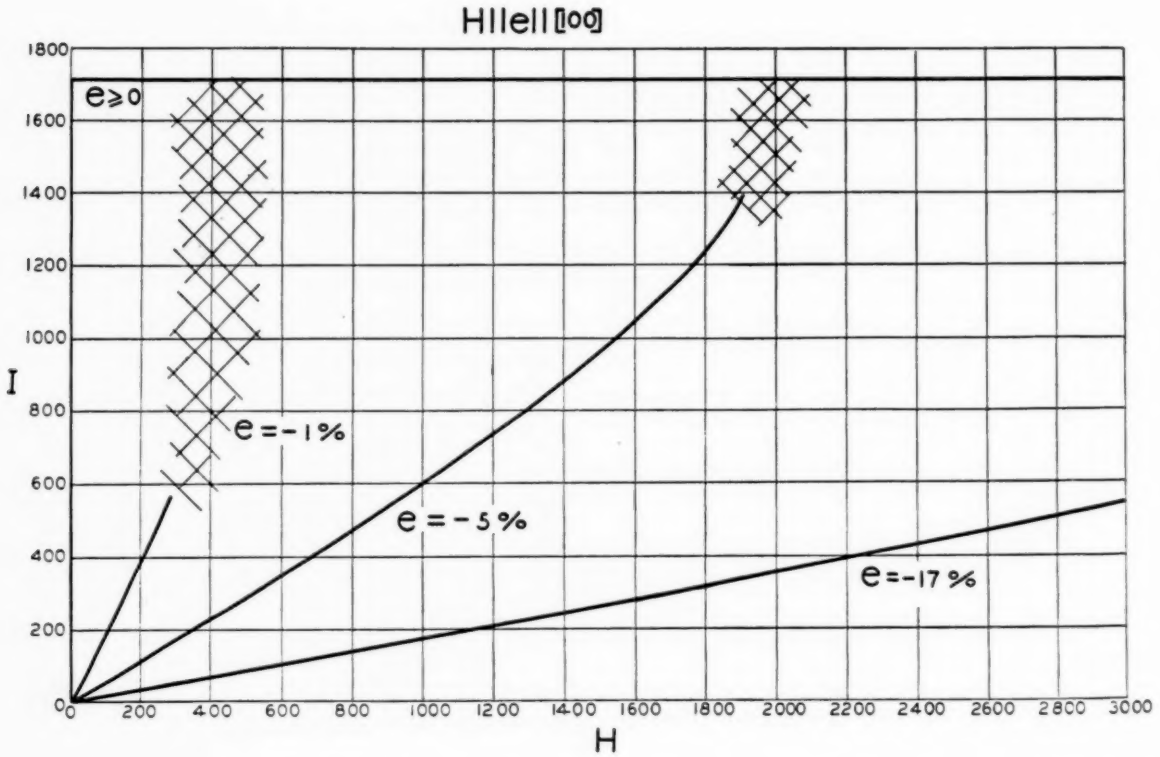

FIG. 10. Magnetization curves for an iron crystal elastically stretched or compressed along a [100] axis by an amount e, the applied magnetic field being parallel to the compression.

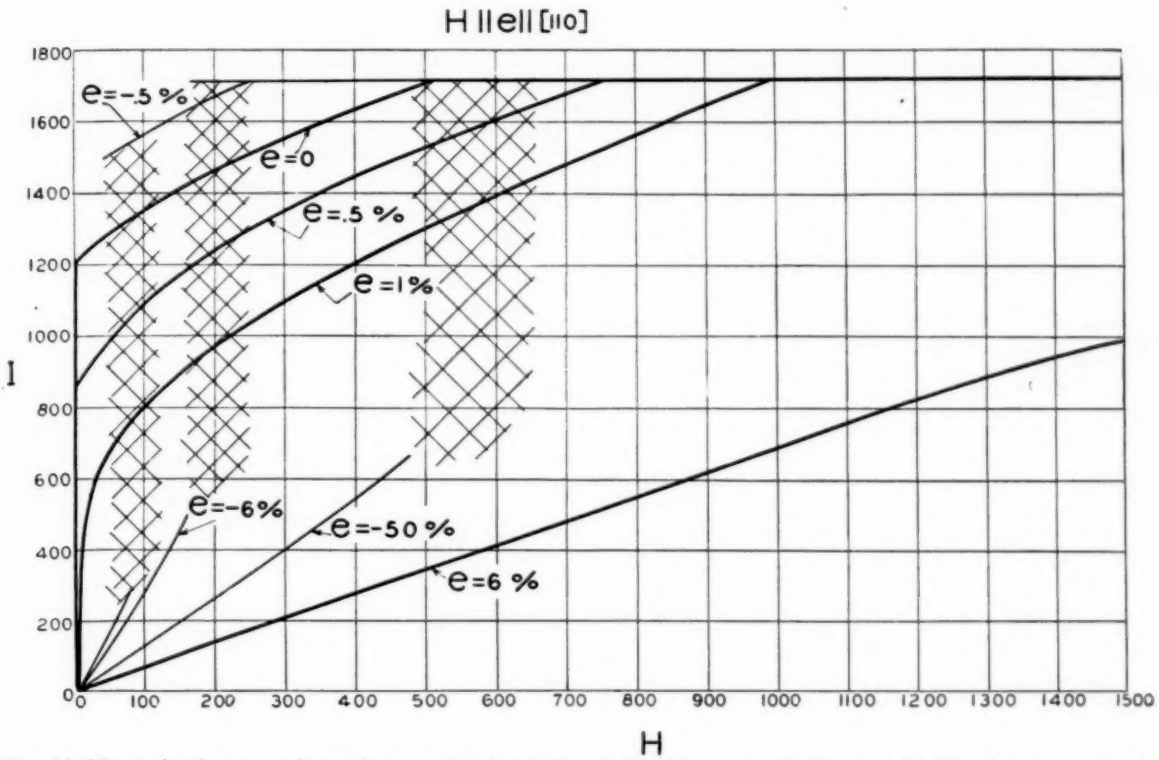

FIG. 11. Magnetization curve for an iron crystal elastically stretched or compressed along a [110] axis by an amount e, the applied magnetic field being parallel to the elongation.

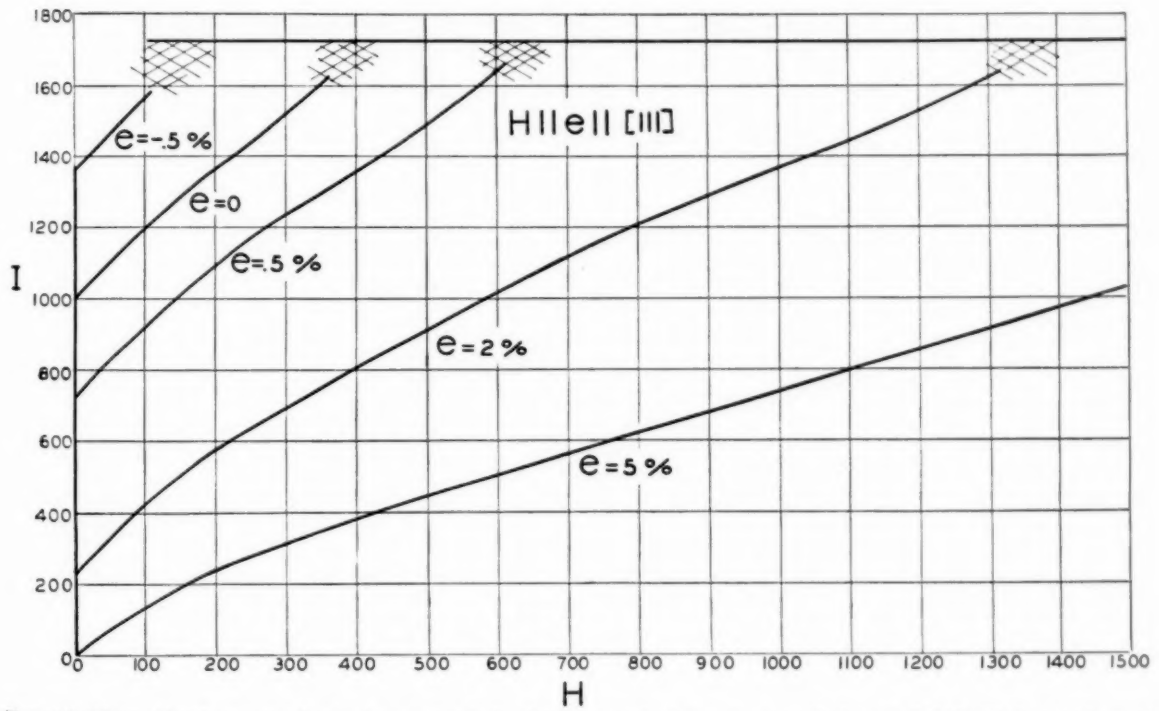

FIG. 12. Magnetization curve for an iron crystal elastically stretched or compressed along a [111] axis by an amount e, the applied magnetic field being parallel to the compression.

The formulae derived from Eq. (1) representing the curves drawn in Figs. 10–12 are:

$e\|\|[100]$—*Fig. 10.*

$$H=aI+bI^3,\quad a=(3eK_1+4c)/I_w^2,\quad b=-8c/I_w^4. \tag{4}$$

$e\|\|[110]$—*Fig. 11.*

For $e>0$ and for the upper portion of the curve for which $e=-0.005$

$$H=aI+bI^3,\quad a=(3eK_2-4c)/I_w^2,\quad b=8c/I_w^4, \tag{5}$$

for the lower part of the curves corresponding to $e<0$

$$H=aI+bI^3,\quad a=[(3/2)(K_1+K_2)e+4c]/I_w^2,\quad b=-6c/I_w^4. \tag{6}$$

The shape of E_θ should be examined in some detail before applying this formula for small values of e.

$e\|\|[111]$—*Fig. 12.*

$$H=\frac{3^{\frac{1}{2}}}{I_w}\frac{2c\sin\theta\cos\theta[2\cos^2\theta-\sin^2\theta]+eK_2[\sin\theta\cos\theta+2(\cos^2\theta-\sin^2\theta)]}{-\sin\theta+2^{\frac{1}{2}}\cos\theta},$$
$$I=I_w[(1/3^{\frac{1}{2}})\cos\theta+(2/3)^{\frac{1}{2}}\sin\theta]. \tag{7}$$

Anyone interested in securing casts of the plaster models here illustrated should communicate with the Magnetic Division of the Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

New Techniques in the Cosmic-Ray Field and Some of the Results Obtained With Them*

ROBERT A. MILLIKAN, *California Institute of Technology*
(Received February 16, 1933)

EACH new field of scientific study goes through a period of development which may be likened to the development of a man child. Up to the age of six or seven a boy interests everybody intensely. In babyhood he is new and sweet and altogether charming because of the awakening qualities which bloom forth as he becomes a real person, and from then on up to seven or eight he is intensely interesting because he is revealing day by day what kind of a person he is likely to be. Then from say eight to thirteen he goes through a period in which he is in general best described as a whining brat who knows no law, is always against the government, and has no real friend except his mother. From about thirteen on he begins to find himself as a member of the human family, and by the time he is twenty-one is ready to don the toga and be admitted regularly into the ordered society of adults.

It is now just over twenty-one years since Gockel[1] made the balloon ascent which revealed the new and quite unexpected fact that there were penetrating rays at an altitude of 4 kilometers of greater intensity than at the surface, i.e., at a height to which no rays could possibly reach, as everybody then knew, if they came from the earth. The cosmic rays ought therefore to be now of age. But the war robbed them of six or seven years of their life, and this may account for the fact that they are just now emerging from the lawless, friendless period into the period of orderly, recognized behavior. But until this emergence is more or less complete, the less public attention is focussed on the "ugly brat" the better it is both for him and for the public. In the lawless or controversial state, before the simple facts have been determined and sufficiently checked to become generally recognized by physicists, the child is of no interest or value to the public. Better for him to have no friend except his scientist mother until he learns to behave himself.

I shall then have little to say today about the controversial aspects of the cosmic-ray field. These will not be controversial long, nor are they anything like as controversial now as the public, for some reason, seems to think. Indeed so far as all the major and really significant facts of observation are concerned, there is general agreement now. There are differences as regards accuracy of measurement and there undoubtedly are differences in interpretation, but so far as I myself am concerned, nothing has happened which alters in any essential or fundamental way the views which I expressed in my last comprehensive report written more than a year ago and printed in the Proceedings of the International Electrical Congress[2] held last July in Paris. I hope very much that anybody who is really interested in the subject will take the pains to read that report before expressing or even forming an opinion, for within the past ten months the American newspapers have been quite consistently misunderstanding and misrepresenting my findings, and I suspect that even some of my physicist friends, who have been too busy with their own work to look up the facts, have been pretty thoroughly misled by incorrect reports.* However, I shall not consume precious time by making the necessary corrections now, but content myself with the mere statement *that the present report is to be regarded as a supplement to the aforementioned one*, for that report, insofar as it goes, will actually stand today with scarcely a change beyond the deletion of a single line which represents merely a slip that should have been deleted anyway, even if no further work had been done (see below). I shall indeed present today new experiments, new techniques, and new results, but these have actually served in the main merely to confirm formerly expressed views, though adding some new and important experimental facts, especially in the fields of energy measurements and of geographical distribution. So far as possible, too, I shall confine myself to results which have been so fully checked and so often repeated that they will now meet, I think, with general acceptance; for this is the stage at which they become both of interest and of value to the public.

The first important and non-controversial fact is that the cosmic rays ionize through the mechanism of the passage

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* Address delivered at Atlantic City on December 30, 1932, as part of a symposium on cosmic rays.

[1] A. Gockel, Phys. Zeits. **10**, 845 (1909); **12**, 595 (1911).

[2] Etat Actuel de nos Connaissances sur le Lieu et le Mode de Production des Rayons Cosmiques, Congrès International d'Electricité, 1932. See also Annales de Institut H. Poincare.

* Even A. H. Compton (Phys. Rev. **41**, 682 (1932)) altogether erroneously reports Bowen and myself as finding but 6 ions at 16 km, and then draws conclusions from this fictitious number which have not the remotest relation to our findings. We actually have never made any estimate as to the ionization at 16 km. Our only statement has been that our flight "seemed to give the *mean* value of the ionization between 5 km (where the value is 15 ions) and 15.5 km as 46 ions." For three years we have repeatedly stated that up to 9 km Kolhörster and ourselves are in substantial agreement so that Dr. Compton's observations at about half that height have not the remotest bearing on 16 km values.

with speeds approaching that of light of charged particles which shoot through electroscopes or other observing instruments and ionize in the well-known fashion of electron rays. In the term electron rays I shall include both positives and negatives, i.e., protons and negative electrons. What seemed to Bowen and myself unambiguous proof of this mechanism was first worked out in the spring of 1931, this proof being found in the observed pressure-ionization relations in pressure electroscopes. We did not publish our findings until I had worked out in July and early August, 1931, also the predicted influence of diurnal changes in temperature upon the observed ionization within a pressure electroscope. When these also checked we sent our findings to *Nature*, which published them in the October 3d issue, 1931, but on September 14th I had presented them orally to Steinke and, a few days later, to Hoffmann in Europe, who at once agreed with our conclusions. Also, a short time after our first publication Bennett, Compton and Stearns, who had independently reached similar conclusions, published their findings, so that, so far as I know, this conclusion, namely, that the cosmic-ray ionization that we observe at the earth's surface is due to high-speed charged particles, is now considered as definitely proved. At least it seems to be universally accepted.

However, the very significant fact that *proton* rays, as above stated, as well as negative electron rays, are the immediate ionizing agents and in something like the same proportions was first brought to light in September and October, 1931, by Carl D. Anderson's measurements[3] on the curvature of these charged-particle-rays in a very powerful magnetic field with the aid of a special vertical Wilson cloud chamber devised by himself and the writer more than two and a half years ago, and permitting 6-inch ray-tracks to be obtained in a uniform magnetic field of strength up to 18,000 or even 20,000 gauss. This is one of the new techniques mentioned in the title and one that extended the range of the measured kinetic energies of charged particles from about 15 million volt-electrons, the limit prior to 1931, up to the order of from two to four billion (10^9) volt-electrons, where it now is. The possibilities of measurement go even higher but no higher energies have been found. Also much caution must be used in studying these nearly straight tracks because of minute sudden changes in direction which sometimes appear. For example, we have cases of nearly straight tracks which seem to show a very slight positive curvature before traversing a lead block a centimeter thick and a slight negative curvature after so doing—an obviously secondary influence of some kind, probably a minute deflection due to a close encounter and not a real curvature at all, and of course such an influence may produce either an apparent increase or decrease in a curvature.

But that positive electrons or proton rays constitute something like half of the immediate ionizing rays, and that some 15 percent of these positive ray tracks are associated with negative ray tracks starting from the same center *constitutes the strongest sort of evidence that both tracks arise immediately from the disintegration of the nucleus of an atom which has been hit by a primary ray of some sort*, in other words, that the *immediate ionizing agents in the cosmic rays are themselves secondaries released from the atoms of the atmosphere by non-ionizing primaries.* I say non-ionizing primaries because we have placed strips of lead a centimeter thick in the middle of the cloud chamber and have repeatedly directly observed ionizing tracks, some times negatives, some times positives, some times both, simultaneously to spring out of the lead when no visible ionizing track enters the lead.[3] This is direct, visible proof of what Hoffmann, Geiger and others long ago showed by placing thin lead sheets above a cosmic-ray electroscope and noting that the ionization in the electroscope was increased instead of decreased by the interposition of the lead, a phenomenon long known with gamma-rays and meaning merely that new secondary charged particle rays are created in the lead by the absorption by the atoms of the lead of the incoming gamma-rays.

Dr. Workman, one of the National Research Fellows in our laboratory, has recently completed an elaborate study of the ionization produced in an electroscope by the hardest gamma-rays as a function of the thickness of a given substance (expressed generally in terms of number of electrons per square centimeter) interposed between the source of the gamma-rays and the ionization chamber. Each material, of course, has its own characteristic curve. If the aluminum curve, for example, is being plotted and successive sheets of aluminum have already been introduced, and if, from a given thickness on, lead sheets are used in place of aluminum, the new points at once leave the characteristic aluminum curve, rise above, then fall below it, and slowly move over to the characteristic lead curve, and reach it as soon as the secondaries released from the originally interposed aluminum sheets are no longer able to get through the added lead sheets. Now, Schindler[4] in Steinke's laboratory has recently published exactly the same sort of curves taken with cosmic rays instead of with gamma-rays, and has obtained exactly the same relation that Workman has obtained with gamma-rays, thus demonstrating again and in a new way that precisely as in the case of gamma-rays the ionizing cosmic-ray-particles are indeed secondaries released by incoming non-ionizing primaries.

But the third and perhaps the most complete demonstration of this conclusion is furnished by Carl Anderson's measurements of the energies of the actually observed cosmic-ray particles; for these measurements show that the majority of these energies lie below 600 million volts, Dr. Anderson and I having published the estimate that not more than a tenth of these tracks reach appreciably above the billion (10^9) volt range.[3] But now we know with great definiteness and great certainty, too, the maximum distance of penetration of billion volt-electron rays through the atmosphere; for such rays, be they positives or negatives, (for at these energies the differences are small) make at least 30 ions per cm of path (45 ions seems now a better mean), and each ion removed from the molecules of air

[3] Millikan and Anderson, Phys. Rev. **40**, 325 (1932); and C. D. Anderson, Phys. Rev. **41**, 405 (1932).

[4] Heinz Schindler, Zeits. f. Physik **72**, 625 (1931).

represents an expenditure of 32 volt-electrons of energy; or such a billion volt-electron as we are considering, and in the case of electrons the same is true of all lower speeds so long as the energy is as high as a million volts (in the case of protons the penetration at low speeds is much less)—loses at least a thousand volts per cm of air path, which means that the maximum range of a billion volt-electron in air cannot be more than a million centimeters or 10 km, more accurately 9.6 km. Indeed Heisenberg[5] makes it but a third that much for billion volt particles. But the depth of a homogeneous atmosphere of the density existing at ordinary temperatures and pressures is 1033 divided by 0.00117 and therefore equals 8.8 km. In other words, a billion volt-electron, if it happened to come in normally to the earth surface, might possibly just get down to sea level and then pass through a roof and an electroscope-wall having a combined thickness equal to a cm of brass. Since the rays come in from all directions, even if all of them were billion volt-electrons, a wholly negligible number of them could possibly reach such an observing chamber. *Since something like nine-tenths of the actually observed ionizing rays have energies under this value, nearly all of the rays observed in such a chamber must then be secondaries, not primaries.* This conclusion seems to me altogether inevitable from the foregoing facts alone. The only possible escape is to say that our measurement of the energies is wrong. It might be slightly wrong in the higher volt range, but it cannot be wrong in the only significant range which is the lower volt range, as anyone can see if he will examine our photographs. Further, Kunze[6] in Fuchtbauer's laboratory in Rostock, has duplicated our measurements in Germany and gets the same distribution of energies as we do. He lists a negligible number of energies up to 4 or 5 billion volts, but, as heretofore indicated, this listing perhaps represents less caution about his high energy measurements than we use, though this is of course quite unimportant for our present considerations.

So far as I can see then the only escape from this argument that these ionizing particles observed at sea level originate practically wholly in our atmosphere is not only to deny the validity of these direct measurements of energies but to postulate, as some have attempted to do, incoming charged particle energies at least ten times, or even a hundred times, higher (10^{10} or 10^{11} volts) for the usual calculations require these energies if the rays are to get through the earth's magnetic field into the equatorial regions at all. This postulate clashes head on and altogether disastrously both with the observed distribution of the cosmic rays in altitude and in azimuth (inclination with respect to the vertical). For 10^{10} volt or 10^{11} volt incoming rays of this sort will produce an atmospheric ionization *very nearly independent of altitude*, instead of increasing very rapidly as the facts require; and as to azimuth, *such rays would produce a uniformity of distribution* of the observed ionization at sea level over the whole celestial dome. But for at least seven years I have been testing this last point in mountain valleys and basins, and I have never found any measurable decrease in the observed ionization when the horizon was screened by mountains up to 30 degrees or even 40 degrees from the horizon. In other words, practically all the rays come in at sea level through a vertical cone of apex at the observer and of 100 degrees or at most 120 degrees opening.

But I am perhaps spending time unnecessarily upon the point of the atmosphere origin of the observed ionizing cosmic-ray particles, for I do not see how it can be doubted for a moment by any one who is at all generally familiar with cosmic-ray facts. There is, however, one further closely related point which should be mentioned. For the main facts which have at any time led anybody to postulate incoming electrons of an energy of 10^{10} or 10^{11} volts are, first, so-called Geiger counter coincidence measurements on absorption coefficients, and second, the aforementioned geographical distribution of the rays. With respect to the first, I have been pointing out for two years in Pasadena seminars, in the Rome congress on nuclear physics in October, 1931, in New Orleans last Christmas at the A.A.A.S. meeting, and in the report for the Paris Electrical Congress, that these counter experiments never in my judgment actually measure the absorption coefficients of anything. I shall presently show that no appreciable number of these observed ionizing particles ever go through more than 30 cm or at most 60 cm of lead, and yet both Regener and Cameron and I have proved that the cosmic rays penetrate through the equivalent of more than 20 feet of lead. These figures cannot both be correct without carrying with them the conclusion that the primary rays at sea level and below are not charged particles. The mechanism of these coincidences is, I think, as follows:

When two counters are separated only by a foot or two of interposed air the coincidences are due indeed wholly to these observed electrons (using now this word to cover both negatives and positives) which shoot through both counters. When, however, 15 cm of lead are interposed between the counters, as in Mott-Smith's experiments, the electrons of energy five hundred million volts or more, of which there are actually a considerable number, do indeed shoot in succession through the upper counter the lead and the lower counter just as is usually assumed: *but the number of coincidences thus produced is now augmented by new coincidences due to the practically simultaneous emission of a succession of secondary particles released along the path of a photon by Compton and other encounters*, the chance for the emission of such secondaries being now enormously increased by the large amount of new matter interposed between the counters. The result is that the number of coincidences with the interposed lead is very much larger than that which corresponds to the absorption coefficient of the charged particles that get through. Messrs. Pickering and Sharp in our laboratory have just now obtained certain confirmations of the correctness of this explanation. It will be seen that if this view is correct these so-called absorption coefficients when thick layers of matter are interposed mean then nothing at all, and the conclusion about particle energies that have been drawn from them are quite invalid. The conclusions to be drawn from latitude effects will be treated below.

[5] W. Heisenberg, Ann. d. Physik **13**, 430 (1932).

[6] Paul Kunze, Zeits. f. Physik **79**, 203 (1932).

The foregoing interpretations gain further support from the new measurements made in the Norman Bridge Laboratory by Carl Anderson on the actual losses in energy experienced by cosmic-ray secondary electrons in going through lead sheets one or more centimeters thick. These measurements are upon the changes in curvature of the same electron tracks (plus and minus) above and below strips of lead a centimeter thick through which they have passed. The average loss in energy is 35 million volts per centimeter, which agrees within less than the uncertainty of measurement with Heisenberg's computed value of 39 million volts per centimeter.[5] It will be seen from this that a billion volt ray has a range in lead of but 30 cm. The great majority, then, of all coincidences obtained through more than this thickness of lead are due if this theory is correct to successive secondaries released along the path of a photon.

Measurements of the type I have been considering in the foregoing paragraph yield other important information; for *even the straightest of these tracks always show measureable changes in direction in traversing the lead.* The statistical way in which these deviations vary with incident energy furnishes a new way of measuring energies, supplementary to the method of magnetic-deviability, and applicable to higher energies. This method alone seems to show that no tracks corresponding to energies of 10^{11} or even 10^{10} volts are actually present among those thus far worked with. Really quantitative conclusions, however, must await fuller statistical data upon such energy losses in traversing lead.

With all these lines of approach, and still others to follow, the two conclusions that seem to me no longer controversial are thus far (1) that the observed ionization at sea level is due to charged particles, and (2) that certainly more than nine-tenths of these particles are secondaries formed in our atmosphere. A third thus far non-controversial result has to do with the general nature of the curve representing the way in which the ionization varies with altitude. I have repeatedly pointed out for the past two years, both in speech and in print, that the curve obtained by Dr. Cameron and myself relating the observed ionization to depth beneath the top of the atmosphere and carried by us with great accuracy up nearly to 5 km runs sufficiently closely into Kolhörster's balloon observations, which he carried up to 9 km. It also runs into the more accurate airplane observation up close to 9 km recently made by Mott-Smith and Howell[7] and Millikan and Neher (see below). In other words, Kolhörster and ourselves are in reasonably close agreement up that far. I have further based the conclusion that this exponential rise, observed by all of us, and reaching in its upper part a value close to $\mu = 0.6$ per meter of water could not possibly continue to the top wholly upon the integrated value of the ionization in the 15.5 km balloon flight with self-recording instruments which Bowen and I made in 1922, and I have repeatedly drawn the important conclusion from this and other phenomena that the incoming rays could not be in complete equilibrium with their secondaries upon entering the atmosphere, since incoming rays in such equilibrium should yield such a continuous exponential rise. *The absence of this exponential rise, and of the equilibrium of the primary beam with its secondaries upon entering,* is the sole conclusion which I have ever drawn from our 1922 flight. If the entering rays are *entirely unmixed* with secondaries upon entering, i.e., if they constitute a pure photon-beam, there should of course be a maximum in the depth ionization curve somewhere on the way to the top, and a year or more ago when Piccard reported a lower observed ionization at 16 km than at 9 km, I thought that this maximum must be found within those limits and so stated, chiefly on the basis of Piccard's briefly-reported findings, in my review for the Paris congress. This is the one line that should now be deleted from that review since Piccard has now in his final report[8] changed his judgment about these two readings. But I further reported in that review that current cosmological theories "seemed to lead to rays which should be in equilibrium with their secondaries (particle rays) upon entering the atmosphere; that *one must then regard this question as not yet settled*" and that Bowen and I were repeating these high balloon flights for the sake of get-more accurate data near the top of the atmosphere, upon the degree of purity, or freedom from secondary particle rays, of the incoming beam.

With the second of our new techniques, for which Dr Neher's skill is largely responsible, and the cooperation of the Weather Bureau, which is also very important, Bowen and I have been repeating then during the past summer our high balloon flights with self-recording instruments, and in the meantime Regener[9] has succeeded in getting one such flight, too, in which he reached an even higher altitude than ours, his altitude record being 28 km while ours is 26 km, though the returns from our last flight are not yet in, and we of course hope that it reached his altitude or better. However, the two flights that are already in and computed check reasonably Regener's up to 20 km, where our electroscope records stop, and all three of these flights seem to confirm the conclusion of lack of equilibrium which we drew from our 1922 flight, though the temperature effect on the electroscope used in 1922 now turns out to have been considerable. How beautiful is the new electroscope technique in the matter of freedom from temperature effects is shown by the fact that a change in temperature from minus 77 degrees C to plus 23 degrees C causes a change of not over 2 percent in the observed readings in our test chamber.

This lack of equilibrium of the incoming rays with their secondaries,—a subject discussed more fully in the report to the Paris Electrical Congress—is attested first by the shape of the depth ionization curve as found now both by Regener and by Bowen and Millikan, for this curve is not even concave upward as the upper part of the atmosphere is traversed as it should be, and very strongly so for rays coming in from all directions, in case these rays are in equilibrium with their secondaries. Instead of this the curve is actually found to have bent over so that it is

[7] Mott-Smith and Howell, Phys. Rev. **42**, 314 (1932).

[8] A. Piccard, Comptes Rendus **195**, 71 (1932).

[9] E. Regener, Naturwiss. **20**, 695 (1932).

somewhat concave downward. It is attested in the second place by the fact that the ionization at the highest point reached (computed by assuming that the coefficient of absorption actually found by all of us, Kolhörster, Regener, Bowen and Millikan, Mott-Smith and Howell, at about 9.0 km, namely about 0.6 per meter of water, maintains its value unchanged to the top, as it should for incoming rays in equilibrium with their secondaries) is actually not half the computed value, the computation of course being made for the actual case of rays which come in from all directions. Further, if the observed coefficient 0.6 is the composite result of rays of different hardnesses, like helium rays, oxygen rays, etc., as Cameron and I have suggested, the discrepancy with the observed ionization becomes much greater. Regener himself, then, draws from his curve precisely the conclusions which we drew from our 1922 data, as well as from our present data, so that the whole field of ionization at very high altitudes is one in which there is as yet no disagreement either as to experimental findings or as to conclusions drawn therefrom by the observers themselves. It should be noted in this connection that the discovery that the secondaries are positives as well as negatives means that even with a quite small admixture of incoming particle-secondaries—though no approach to equilibrium—these positives, released from the nuclei of atoms by the relatively soft incoming primaries which seem to exist in the upper layers, say of 27 million volt energy, would ionize heavily and thus tend to push up the maximum in the ionization-altitude curve to close to the top of the atmosphere. The data close to the top are, however, not yet reliable enough to make quantitative conclusions possible.

But why is it so important to determine whether the incoming rays are in equilibrium with their secondaries or not? Because, if the cosmic rays originate in the stars they should be in such equilibrium, the primaries being mixed with secondary electron rays just as they are at sea level, and if they are not in such equilibrium, then the conclusion that the primaries originate in interstellar space gains added support, though even so no definite proof, since even if they do so originate they might still be in equilibrium (see above). In any case the incoming rays should be mixed *to some extent* with their secondaries, as I pointed out in 1931, since they must at least come through some of the matter, which small though it be, is distributed throughout space. I also pointed out in the paper written for the Paris Congress, before latitude effects had become in any way a controversial subject, that "On ne peut se reposer entièrement sur ces seules indications"; that new light should be thrown upon this important question by looking more carefully for such latitude effects, especially at high elevations and high latitudes; for at sea level under no assumptions which seemed either likely or natural could the secondary rays make their effects felt save as they had energies much greater than a billion volts, and no very considerable number of such energies were either then or now thought to exist. In other words, practically all such secondary incoming electron rays would in any case, no matter where they entered the atmosphere, be filtered out before the earth's surface was reached. But, at an elevation of seven kilometers, for example, or 23,000 feet, secondary entering rays of energies greater than 400 million volts, and many such were known to exist, might make their effects felt in electroscopes so far as penetrating power alone was concerned, and according to my own reasoning and Epstein's calculations[10] the earth's magnetic field should let these high altitude effects through in the high magnetic polar latitudes, but keep them out of the equatorial magnetic latitudes.

I did, indeed, suggest in the Paris paper that incoming secondary charged particles might produce latitude effects even in temperate latitudes through the possible agency of photons arising from the nuclear impacts of such high-speed electrons plunging through the upper part of our atmosphere, and since no such latitude effects were found between Pasadena, California and Churchill, Manitoba, the very region in which such effects were to be expected, I stated that there seemed to be as yet no evidence that the incoming rays were mixed in any measurable degree with their secondary electron rays. This line of approach involves the assumption that very penetrating gamma-rays can be produced by the passage of high-speed electrons through air, an assumption pretty certainly contrary to fact, for, first, although very soft gamma-rays are indeed produced when K electrons are knocked out of atoms by high-speed bombarding electrons, and although somewhat harder gamma-rays might be occasionally produced by similarly knocking out nuclear electrons, I think no gamma-rays capable of penetrating kilometers of atmosphere, as would be necessary if such secondary gamma-rays become observable at sea level, are to be expected from the plunging of high-speed electrons through the light atoms of the atmosphere. The energy available from the mere rearrangement of the parts of such a smashed atom is wholly inadequate. Even if such secondary gamma-rays might thus be produced they could not account for Carl Anderson's observed effects no matter what the energy of the incoming particles, *for his ray-tracks in the great majority of cases come in from above, while 10^{10} volt electrons shooting through the atmosphere should produce at the earth's surface photons shooting out equally in all directions from the bombarded nucleus in case it be assumed that they can produce such high energy photons at all.*

Nevertheless, if the incoming rays are actually mixed to any appreciable extent with their secondary electron-rays of the observed energies the effects of the latter should of course be observable at high altitudes *in polar latitudes* and absent in the equatorial latitudes, and accordingly more than a year ago, i.e., in 1931, I laid before the Carnegie Corporation of New York a definite and detailed program for the carrying out of this high altitude exploration program and also described it explicitly in the aforementioned report for the Paris Congress long before any latitude controversy was ever dreamed of. I was not primarily interested in further sea-level observations because, first, the foregoing reasoning showed that if any magnetic latitude effects could be found at sea level they would of necessity be small, and second, Cameron and I

[10] Paul S. Epstein, Proc. Nat. Acad. Sci. **16**, 658 (1930).

had in 1927 carried sea-level observations from latitude 34 north to 17 south and found no variation which was outside the limits of our experimental uncertainty, which we estimated at 6 percent. Further, the next year I had helped Dr. Gish to calibrate electroscopes which were taken on the good ship "Carnegie" and with which 500 observations were made in the equatorial latitudes from 20 degrees north to 20 degrees south, and an equal number from 20 degrees to 60 degrees south, and also half that number from 20 degrees to 60 degrees north, without bringing to light any sea-level latitude effects which were greater than the observational uncertainty which I estimated again, upon privately getting this data from Dr. Gish, to be of the order of 6 percent. However, these Carnegie observations showed, if anything, slightly lower equatorial values than higher latitude values, the mean of 507 readings between 20 north and 20 south being 3.32 ions/cm³/sec., of 262 readings between 20 north and 60 north being 3.39, while the mean of 509 readings between 20 south and 60 south was 3.44 ions/cm³/sec. The estimated zero was here about 2 ions/cm³/sec. The readings in the equatorial belt are indeed 5 or 6 percent lower than those in the north temperate belt, but those in the south temperate belt differ from those in the north temperate by nearly as much. Further all of these differences might have been due to barometric differences, for which at that time dependable correction could not be made. It was for these reasons that in 1930 I made an elaborate and accurate comparison of sea-level intensities at Pasadena (lat. 34) and at Churchill within 700 miles of the North magnetic pole, for here I expected the maximum differences to appear, but I found no difference that exceeded my observational uncertainty which was stated in these measurements to be not over 1 percent.

For these 1930 observations from latitude 34 northward both at sea level and on mountains were taken with improved, very sensitive electroscopes and were very much more accurate than our South American ones. Bennett and Dunham,[11] as well as Neher and myself, have this last summer completely confirmed these findings, not only at sea-level but on mountains from five to nine thousand feet high, so that there is now entire agreement upon the only point having to do with latitude effects upon which I have at any time been insistent or even claimed to have made accurate measurements (see also below) namely that *from Pasadena northward, within the limits of our observational uncertainty, there is no effect of latitude so far as observations on terra firma, high or low, have gone.* It is to be noted, too, that according to Epstein's[10] and Lemaitre's and Vellarta's[12] calculations, these high latitudes, north or south, are the only regions in which latitude effects on intensities can be expected as a result of the action of the earth's magnetic field on incoming charged particles of the observed energies. There is no doubt at all about the abundance of secondary charged particles up to energies of 500 million volts. If the effects of such secondary incoming rays do not appear about the magnetic poles, the alternative inferences will be (1) that the incoming primaries are not appreciably mixed with their magnetically deflectable secondaries, or (2) that we have not extended our observations to high enough altitudes in the atmosphere or to high enough latitudes to bring these effects to light, *for the earth's atmospheric skin is so thin that no latitude effects of secondaries formed in our atmosphere can be expected.*

A third possible hypothesis might be made, namely, that the earth's magnetic field, like the sun's, does not extend out as far into space as that of such a theoretical magnetic dipole should. This would shift the expected effects of the incoming secondaries to lower latitudes, where we should find them if only we carry our observations high enough.

As to the mere observational facts at sea levels divorced from all theorizing, it should be reported that Clay[13] has two or three times during the past five years reported from 10 to 20 percent of equatorial lowering on voyages from Batavia to Europe via the Suez Canal, lowerings which he has related to magnetic latitudes and that A. H. Compton[14] has reported similar results obtained in the western hemisphere. On the other hand, E. Oeser[15] of the University of Göttingen has just repeated the sea-level observations between latitude 50 degrees north and latitude 7.1 degrees north (Hamburg to the Panama Canal) and reports no change whatever in his electroscope No. 1, that was airtight, but a lowering of 17 percent in the equatorial regions for a second electroscope (No. 2) which was definitely proven to be leaking and which therefore contained more rarefied air in the hotter areas than in the colder ones. But the most significant and dependable measurements of all have just been made by Dr. Neher, who has carried one of our new sensitive recording electroscopes by sea from Pasadena (34 N.) to Mollendo (17 S.) and back without finding at sea level any changes appreciably larger than the limits of the uncertainties indicated above, namely, of the order of 6 or 7 percent. However, the mere uncertain *indications* previously found of about this amount of equatorial lowering are now confirmed by these quite exact and dependable readings, which show an increase in coming from Mollendo (17 S.) to New York (41 N.) of 6.8 percent correct to one or two percent.

With respect to all my former sea-level observations, I have always been very careful to make no other statement than this: First, that "I myself have never been able to find any sea-level effect of latitude which was outside the limits of my observational uncertainty." That statement I shall obviously never have to retract, and it cannot properly be made the subject of controversy. But, further, my estimated uncertainty of 6 percent between Pasadena (34 degrees north) and Mollendo (17 degrees south), and

[11] Bennett, Dunham, Bramhall and Allen, Phys. Rev. **42**, 446 (1932).

[12] Lemaitre and Vellarta, Phys. Rev. **43**, 87 (1933). See also Nature **128**, 704 (1931) for Lemaitre's superradioactive theory of cosmic-ray origins.

[13] J. Clay, Proc. Roy. Acad. (Amsterdam) **30**, 1115 (1927); **31**, 1091 (1928); **33**, 711 (1930); and J. Clay and H. P. Berlage, Naturwiss. **37**, 687 (1932).

[14] A. H. Compton, Phys. Rev. **41**, 111 (1932).

[15] E. Oeser, Zeits. f. Geophysik **8**, 242 (1932).

of 1 percent between Pasadena and Churchill may of course some time have to change, but I think there will be general agreement that with the observations of Millikan and Cameron, the Carnegie Institution of Washington, Oeser and Millikan and Neher all in reasonably good agreement it would be quite premature to change them appreciably now.

But with respect to *high-altitude* latitude effects, as already indicated, I have thought them so likely as to publicly state in several addresses in Europe, delivered in October and November of 1931, and in the aforementioned article written in 1931, that I was undertaking a rather elaborate high altitude latitude survey. The carrying out of such a survey required the development of the second new technique referred to in the title of this paper, for the observations had obviously to be made in airplanes which can hold the same level for long periods, and they had to be as accurate as those made in a laboratory. It is largely Dr. Neher's extraordinary skill which has made the success of this program possible. The instruments are self-registering and work just as well in an automobile or a railway train running over rough roads, or even in a diving airplane, as in a laboratory. They yield the most accurate airplane observations of which I myself have any knowledge, though I have assisted in making many inaccurate airplane tests. They are very much more accurate than any balloon observations made by ourselves, and I think these compare well with the balloon observations made by others. Further, any one who henceforth wishes to check for himself our results need only come to our laboratory and measure up our films, which of course are without prejudice or preconception of any kind.

There are two main results of these high altitude airplane tests that I wish to report. With the aid of Colonel Arnold and the staff at March Field (latitude 34), we took up one of our new electroscopes inside a four-inch lead shield to an altitude of 21,000 feet, or about 7 km, and then we repeated the observations without the lead, so that we now know exactly how much of the rays at each altitude are cut out by the lead, not roughly but quite accurately. At 21,000 feet the ionization inside the lead is less than one-third what it is with the lead removed. This means that more than two-thirds of the ionizing secondary rays existing at that altitude are unable to pass through four inches or 10 cm of lead. This means in turn, since many new secondaries are of course produced within the lead, that very much more than 66 percent, *probably as much as 80 percent of the secondary ionizing rays existing at 21,000 feet, have insufficient energies to carry them through 10 cm of lead, and that means energies below about 350 million volts.* This checks very beautifully our conclusion that practically all the ionizing rays are secondaries produced in the atmosphere, for 350 million volt rays cannot possibly penetrate one-third the thickness of the atmosphere. This way of finding the distribution of the energies of the ionizing particles cannot, I think, be seriously in error. It shows that at least 35 percent of the ionizing particles existing at sea level, to take another example, have energies under 350 million volts and this checks well with Carl Anderson's direct measurement of the distribution of particle-energies. Again, Mott-Smith and Howell's high altitude measurements[7] tell precisely the same sort of a tale, for at 25,000 feet these observers report that a one-inch lead screen cuts off 40 percent of the ionization. This means that certainly much more than half the particle-rays existing at 25,000 feet have an energy under 90 million volts. All these new airplane observations, then, confirm most emphatically the banded structure of the cosmic rays, upon which I have been insisting since 1925. *Indeed, the rapidly progressive softening of the rays with altitude, here brought sharply to light, is I think inexplicable on any charged particle theory as to the nature of the primary rays.*

The other result of the airplane tests relates to the high altitude geographical findings. Exactly the same sort of flights in which the pilot flew for an hour at 10,000 feet, an hour at 14,000, an hour at 19,000, and an hour at 21,000, were made first at March Field (latitude 34, magnetic latitude 50 reckoned from pole position at 70°); then at Spokane (latitude 47, magnetic latitude 64), where the flights were most skillfully made by Major Breene, then at Cormorant Lake, Manitoba (latitude 55, magnetic latitude 75), where Flight Commander Gordon of the Royal Canadian Air Force generously and skillfully flew for us. Also, a similar flight was made in Peru (latitude 17 south, magnetic latitude 2° N.), and still another, with the assistance of the U. S. Army at Panama, 7.1° N., magnetic latitude 24.1 N. In these flights the electroscope is automatically recharged once every 15 minutes, and it is so sensitive that it moves over the 100 divisions of the scale in 15 minutes at sea level. *The Cormorant Lake and the Spokane curves show no differences whatever, and yet this is where the magnetic effect of the earth's field on negative electrons of energies up to 10^9 volts should be most felt.* Its failure to appear there may perhaps be considered as pointing again toward the absence of appreciable numbers of secondary deflectable rays of the above-mentioned, directly observed energies in the incoming beam, but an alternative explanation is that the earth's magnetic field is not as strong as is assumed in the Epstein, Lemaitre calculations.

Quite unexpectedly, however, the results at March Field at 21,000 feet are 11 percent lower than those taken at the same altitude at Spokane and at Cormorant Lake. With respect to the high altitude tests in the equatorial belt, the Peru flight and the Panama flight are in perfect agreement and yield distinctly lower high altitude readings than any of the others, 40 percent lower at 21,000 feet than the Spokane and Cormorant Lake readings. It is interesting to observe, also, that this diminution in the high altitude intensities of the cosmic rays in the equatorial regions actually stands out clearly from the published readings which Cameron and I took in the High Andes in 1926,[16] though we did not then call attention to it, nor ourselves assign to it special significance; for these readings were taken before we had developed sensitive high pressure electroscopes and we were unable at that time to lay much claim to precision. Further, we had taken but a dozen or so under-water readings at Lake Maguilla at an altitude of 15,000 feet when, as indicated in our published article,

[16] Millikan and Cameron, Phys. Rev. **31**, 165 (1928).

leaks developed in our electroscopes. We therefore relied mainly for our latitude findings upon our sea-level readings, of which we had a great many and which were quite free from suspicion as to possible effects of leaks. However, in view of the thinness of the earth's atmospheric skin and the universally assumed character of the earth's magnetic field *no latitude effects due to the earth's magnetic field could possibly be expected at high equatorial altitudes if they failed to appear at sea level.* This is why we based our conclusion as to a lack of a latitude effect chiefly upon our sea-level readings and drew one single ionization-depth curve through all our points taken up to that time at high altitudes both in the northern hemisphere and in Peru and Bolivia and assumed that the points that fell off this curve represented observational uncertainties, though, as any one can now see by looking at them, these points actually do show clearly the differences between readings at a given altitude in Bolivia and in the United States. For our published composite curve embracing all readings taken up to the end of 1926[16] is actually considerably lower at its upper end, e.g., at 7 m beneath the top of the atmosphere, than is the corresponding curve taken in the northern hemisphere either in 1925[16] or in 1931.[17] Indeed, the mean values of the ionization at a depth of 7 m beneath the top of the atmosphere is 16 percent higher in the Muir Lake data than in the Lake Maguilla data, and when we compare the more accurate 1931[17] curve we find just as does Compton, a difference of more than 30 percent at this same altitude. In other words, from this last curve the reading corresponding to a depth of 1 m beneath the surface of Lake Maguilla should have been more than 6 ions instead of the observed 4.1 ions. In other words, the *published Bolivia readings are actually at least 30 percent lower than the readings taken at the same altitude in the central part of the United States.* I have often discussed with others this difference between our curves taken in South and North America, and it was chiefly because of this discrepancy and of the aforementioned readings taken on board the Carnegie that I decided in 1931 to make what I regarded as a crucial test of this latitude question by comparing intensities at Pasadena and at Churchill, the only latitude stretch in which I estimated that the effect of the earth's magnetic field could cause large differences at any altitudes. In a word, then, *the lowering of the observed cosmic-ray intensities at high altitudes in the equatorial regions is consistent with all the high altitude observations which have yet been taken by anybody, so that there is no chance for controversy about this point.* Only at sea level is the observational data not yet in quantitative agreement. In the matter of interpretations there are quite naturally differences of opinion.

With respect to these interpretations it is quite clear that this new high altitude data in different geographical areas cannot easily be brought into consistency merely by invoking the earth's magnetic field, for there are real difficulties which a magnetic interpretation encounters. The first is to explain the fact that the small sea-level dip in intensity occurs only in quite low, i.e., in equatorial latitudes. According to a hypothesis which Epstein and I have considered and which he will presently publish in quantitative form, it is sought to explain this dip as follows: The photon hypothesis as advanced by Millikan and Cameron is adopted to account for the whole of the observed ionization in the equatorial belt, for the earth's magnetic field would in any case prevent the penetration of particles of the observed energies into this belt. But of the ionization observed at sea level between Pasadena and Churchill, only 93 percent would be due to incoming photons while to account for the 7 percent equatorial dip it is assumed that there is a small admixture of charged particles superimposed upon these photons. From Epstein's point of view these particles might be looked upon as having the same relation to photons as beta-rays have to gamma-rays in radioactivity, or they might be secondaries produced by the incoming photons and therefore entering our atmosphere as a beam either in partial or total equilibrium with its secondaries. But to enable the earth's magnetic field to remove them only in equatorial latitudes and leave the sea-level intensities from Pasadena to the pole constant, Epstein is obliged, following his own and Lemaitre's computations, to postulate that these particles have energies as high as from three to eight billion volts. Such particles, however, should have so high a penetration that, in the first place, they should be observable at all angles from the vertical clear down to the horizon, which they do not seem to be, and, in the second place, they should appear in greater numbers than they seem to do in Dr. Anderson's direct measurement of energies.

The third difficulty is as follows: Although the assumed Millikan-Cameron photon hypothesis can take care of the larger part of the enormous rise in the intensity of ionization with altitude, these high energy entering particles must take care of the whole *difference* observed at any and all altitudes between the ionization in the equatorial belt and the temperate belt. This is a difference which near the Equator increases from 7 percent at sea level to 40 percent at 21,000 feet, but since the actual ionization at 21,000 feet is seventeen times that at sea level and the percentage of particle-rays is, as above stated, five times that at sea level, the ionization at 21,000 feet due to the incoming particle-rays alone must be $5\times17=85$ times greater than the incoming-particle-ionization at sea level. But the particle-rays which must produce this sort of ionization are also required to get through the earth's magnetic field and reach the earth's surface between Balboa (latitude 7.1) and Pasadena (latitude 34), and it is this condition that limits their energies to the range from three to eight billion volts. If such high energy rays are to produce anything like the observed ionizing effects, then the particle energy necessary to just get through the earth's atmosphere must be assumed to be some five or six billion bolts, instead of but about one billion as calculated above. This seems to be somewhat higher than the present rather incomplete experimental situation allows. If it should be found permissible the three difficulties mentioned might all disappear.

But there is still a fourth difficulty. Since incoming particle-rays are continually losing energy along their

[17] Millikan and Cameron, Phys. Rev. **37**, 244 (1931).

paths their energy or penetrating power should increase, not decrease, with altitude, but as was shown sharply by the foregoing measurements of Millikan and Neher in their airplane flights made with and without their 10 cm lead shields the mean penetrating power actually decreases rapidly with altitude, being about one-third as much at 21,000 feet as at sea level. This behavior defies any natural interpretation on the basis of incoming charged particles alone, but fits nicely the theory of incoming photon bands made up of He, O, Si, Fe, etc., rays. Now, according to the foregoing hypothesis as to the effect of the earth's magnetic field, the ionization in the equatorial belt is due wholly to such bands of photons, but in the temperate belt, as is shown by the difference between the readings in temperate and equatorial latitudes, as much as 30 percent of the ionization at 15,000 feet arises from the 3 to 8 billion volt incoming particle rays. Hence, at 15,000 feet a much larger percentage of the observed rays should get through the 10 cm lead shield in the temperate and polar belts than in the equatorial belt. Actually Neher and I found by quite accurate airplane measurements in the United States at 15,000 feet 38.7 percent of the ionization inside the 10 cm lead shield that we found outside it and in the equatorial belt Neher got the same way 39.2 percent, i.e., *the rays at 15,000 feet are of very nearly the same mean hardness in Peru as in the United States. In a word, then, both the observed very rapid change in ionization with altitude and the observed lack of effect of latitude upon hardness, or mean penetrating power, especially at high altitudes, present rather serious difficulties to any sort of an incoming-particle theory even though these particles be secondaries which are required to account for but 7 percent of the observed sea-level intensity.*

From my point of view, however, these difficulties would be reduced and perhaps entirely avoided if it might be assumed that the earth's magnetic field does not have the generally assumed strength so that secondary particles of energies more nearly like those actually observed might be mixed, in temperate as well as in polar latitudes, with the incoming photon beam, for the wide distribution of energies among these secondary-particle rays would help in understanding the increased ionization with altitude, which must be attributed as well to the particle component as to the photon component of the rays. If this weaker magnetic field cannot be postulated, nor the low penetrability that Epstein suggests, then there is no further recourse other than to postulate some secondary influence of a non-magnetic sort to account for the observed dip in the equatorial belt. It is barely conceivable that the following hypothesis might have value.

The earth's negative electrical field must be taken as equivalent to an additional resistance to the inflow of negative particles, so that if these predominate, as they ought to do in view of Compton encounters, an increase in the electrical field would result in a pushing down of the curve and a decrease in the field to an elevation of it. Now, water vapor, plus the difference in mobility of newly formed negatives and positives, is presumably the great underlying cause of the electrical separations which result in strong electrical fields in the upper air, and it is in the equatorial regions that most of the water is lifted into the atmosphere and to relatively great altitudes. The absence of an important effect at sea level might then be due to the fact that the rays that get down to sea level are so hard that the influence of the electrical field is negligible in comparison, though not so at the higher levels where the rays are as shown relatively very soft. Clay's strange results between Genoa and Suez might possibly be due to the tropical temperatures existing at higher latitudes here than in the western hemisphere. It should be possible to test the correctness of this suggestion. A few months hence we shall have more and better information upon this point.

The work herein reported has been made possible through a grant received for the purpose from the Carnegie Corporation of New York administered through the Carnegie Institution of Washington, to which bodies I wish herewith to make grateful acknowledgment.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Secondary Absorption and Fine Structure of X-Rays as Observed with a Double Crystal Spectrometer

Several observers have noted, in the case of solids and polyatomic gases, a secondary absorption or fine structure extending for some hundreds of volts on the short wave-length side of x-ray absorption edges in addition to the well-known fine structure in the edge itself. The results of experiments on this fine structure are in good agreement with Kronig's[1] theory of forbidden and permitted zones or energy levels in the crystal lattice. According to Kronig's theory, electrons in an atom of the crystal can not absorb quanta of certain discrete energy values if the initial impulse given to the electron is parallel to a crystal axis. On this basis the maxima and minima of the secondary absorption should be more pronounced when the electric vector of the incident x-rays is parallel to a crystal axis than when it is in some other direction or oriented at random. It is therefore important to test whether or not the secondary absorption is dependent on the degree of polarization of the incident x-rays and on the orientation of the electric vector with respect to the crystal axes of the absorbing screen.

The double crystal spectrometer with its high resolving power should be well adapted for this purpose if a combination of crystals can be found such that the first crystal can act both as monochromator and polarizer for wave-lengths close to an absorption edge of one of the elements in the second crystal. Lindsay[2] has obtained secondary fine structure using one crystal for the double purpose of grating and absorber. Most of the data on secondary absorption have been obtained by the photographic method with a single crystal spectrometer, though Davis[3] and Hull[4] have obtained the fine structure in the main edge itself with a double crystal ionization spectrometer. It is therefore important to have the existence of the secondary absorption confirmed by the latter method. It so happens that the third order glancing angle with the (110) planes of calcite is approximately 45° for the wave-length of the *K*-absorption edge of bromine, thus giving complete polarization, while for second order reflection the polarization is some 75 percent.

One of us (Stephenson) is now engaged in experiments with a double crystal ionization spectrometer to test the effect of polarization on secondary absorption. The first reflection is from the (110) planes of calcite and the second from the cleavage planes of an artificial KBr crystal kindly sent us by Professor G. A. Lindsay of the University of Michigan. Because of the small intensity in the third order, the results so far have been obtained with the first crystal reflecting in the second order and the second crystal in the first, with a cube edge perpendicular to the common plane of incidence. As can be seen from the accompanying curve, preliminary results show a pronounced secondary fine structure on the short wave-length side of the bromine *K*-edge similar to that obtained photographically by others. This curve is a composite curve containing points from several different runs in the (2, 1) position. The scattering of the points is due chiefly to three causes: (1) variation of electrometer sensitivity from day to day for which correction is difficult, (2) temperature changes between runs, (3) the smallness of the current measured, being of the same order as that due to a single alpha-particle. The uncertainty of any one electrometer reading is quite high, being sometimes nearly ten percent of the mean. Several readings are

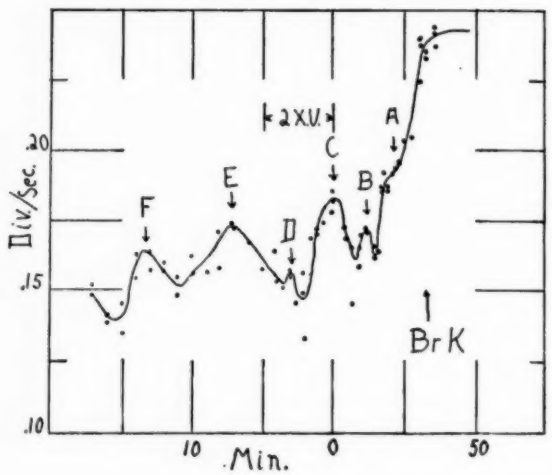

FIG. 1.

[1] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932).

[2] G. A. Lindsay, Zeits. f. Physik **71**, 735 (1931).

[3] B. Davis and H. Purks, Phys. Rev. **32**, 336 (1928).

[4] H. L. Hull, Phys. Rev. **40**, 676 (1932).

averaged for each point on a curve and the curves are repeated several times. All the points are not given in this composite curve, but those given are representative.

The secondary absorption minimum C has been measured four times in the (2, 1) position and twice in the (2, −1) position; E and F have been measured twice in the (2, 1) position. The peak D may be due to crystal imperfections. The fine structure in the main edge at A is quite definite. The data so far obtained are insufficient to establish the effect of polarization of the x-rays on the fine-structure, but they do confirm the results obtained by others photographically. Complete details of the experiment will appear at a later date.

C. D. COOKSEY
S. T. STEPHENSON

Sloane Physics Laboratory,
Yale University,
March, 1933.

Potential Energy of Diatomic Molecules

Recently, in a paper by Ikehara and the present writer,[1] calculated results were presented giving the first-order $^1\Sigma$ energy curves for molecules consisting of two identical atoms, each with an outer s-electron, for various values of the effective principal quantum number. The $^3\Sigma$ energy curves were not given there although enough data were given so that they could be constructed. If one determines the $^3\Sigma$ curves one finds that for $n \leqq 4$ they are of the usual form corresponding to a repulsive force. For $n=5$, the curve has a minimum, however, and if one extrapolates to $n=6$ (which can be done fairly accurately by extrapolating the Coulomb and exchange energy curves expressed as Morse[2] functions) one finds that in this case the minimum is below the asymptotic value at infinity, corresponding to the possibility of existence of a stable molecule. This effect is due to the rapid decrease in the importance of the exchange energy with increasing n. In Fig. 1 these curves are presented together with the $^1\Sigma$ curve for $n=6$.

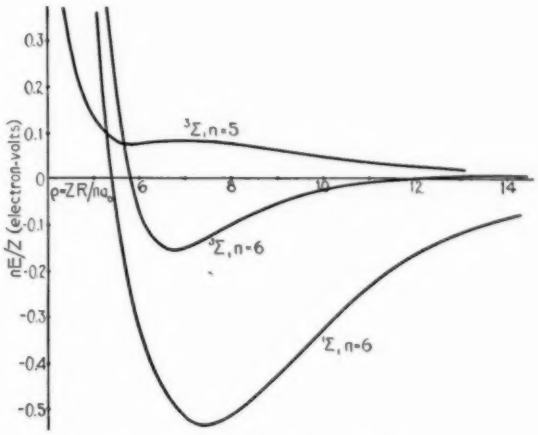

FIG. 1. Interaction energy curves.

The $^3\Sigma$ curves in the diagram are not particularly important in themselves since the corresponding molecules could hardly be obtained under ordinary conditions. However, they are of interest in showing that the first-order perturbation method may sometimes lead to energy curves of the "radioactive decay" type, i.e., having a maximum beyond the minimum. It is quite likely that for certain electronic levels, molecular energy curves similar to those discussed here may occur for smaller values of n, and hence with more pronounced maxima; the minima might be either above or below the axis. Such curves may be of importance in various types of predissociation, even if no rotation is present.

N. ROSEN,
National Research Fellow

University of Michigan,
March 30, 1933.

[1] Rosen and Ikehara, Phys. Rev. **43**, 5 (1933).
[2] Morse, Phys. Rev. **34**, 57 (1929).

On the Permeability of Iron at Ultra-Radio Frequencies

Recently there was published an interesting article by Hoag and Jones[1] who have worked out a method for exactly measuring the self-induction of wires in oscillating fields of wave-lengths between 22 and 64 cm. By this method they determined the self-induction of iron wire, calculated the permeability μ_n, and compared it with my values of permeability μ_k, previously calculated[2] from the resistance of wires at a frequency of the same order. As was the case for my values of μ_k Hoag and Jones find that the permeability μ_n calculated by them greatly diminishes at shorter wave-lengths. On the other hand, their values of permeability are appreciably lower than mine. This can be explained in the following manner. The essential difference between μ_k and μ_n appears in the following equations:

$$\mu_k = (\mu^2+\rho'^2)^{\frac{1}{2}}+\rho' \qquad \mu_n = (\mu^2+\rho'^2)^{\frac{1}{2}}-\rho',$$

where ρ', an essentially positive coefficient, together with the magnetic permeability μ serves to define the magnetic induction B. B is retarded with respect to the magnetic field H through the angle $\delta = \text{arctg}\, \rho'/\mu$:

$$B = \mu H_0 \cos(2\pi t/T) + \rho' H_0 \sin(2\pi t/T),$$

[1] J. Barton Hoag and Haydn Jones, Phys. Rev. **42**, 571 (1932).
[2] W. Arkadiew, Phys. Zeits. **14**, 561 (1913); Ann. d. Physik **58**, 105 (1919); Zeits. f. Physik **28**, 11 (1924).

where T is the period. The value μ_n determines the coefficient of refraction n of electromagnetic waves in a ferromagnetic metal, while μ_k determines their coefficient of absorption[3] k:

$$n=(\sigma T\mu_n)^{\frac{1}{2}} \text{ and } k=(\sigma T\mu_k)^{\frac{1}{2}}.$$

In practice μ_k is usually calculated from the resistance of ferromagnetic wires to an alternating current and μ_n from their self-induction. The values μ_k, defined by me, were calculated from the resistance determined from the coefficient of absorption of waves in parallel wires. In another paper[4] I determined the magnetic permeability by a method which consisted in comparing the coefficient of reflection of the waves from a coarse Hertzian grating of magnetic wires, with the coefficient of reflection from a grating of non-magnetic wires of the same diameter and resistance.

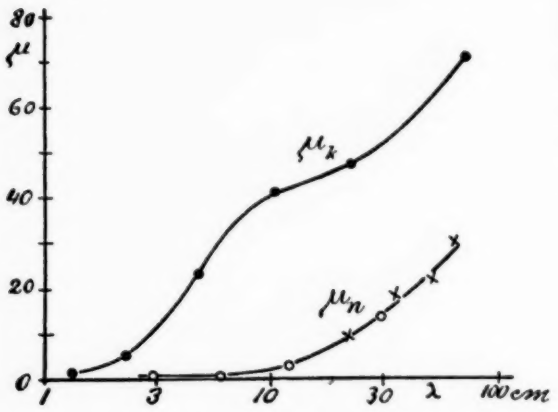

FIG. 1.

This method allows one to calculate the value of μ_n and to compare it with μ_k obtained by the method of absorption of the waves in wires.[5] The results observed by me for λ between 1 and 73 cm for a wire 0.0245 mm in diameter, are shown by circles in Fig. 1. The values of μ_n obtained by Hoag and Jones are shown by crosses. They relate to a wire 3.18 mm in diameter. The concordance of the results of Hoag and Jones with my values is better than expected. We see from the above, that the values obtained by them for μ_n were bound to be smaller than my values for μ_k. We see also, that the permeability of iron really decreases, approaches 1 at $\lambda=1$ cm, and approaches the value corresponding to thermal and optical frequencies.

W. ARKADIEW

J. Cl. Maxwell Laboratory,
(Moscow Magnetic Laboratory),
University,
January 21, 1933.

[3] W. Arkadiew, Phys. Zeits. **14**, 928 (1913).

[4] W. Arkadiew, Ann. d. Physik **45**, 133 (1914).

[5] W. Arkadiew, Ann. d. Physik **81**, 661 (1926); Table IV, Fig. 3; Festschrift d. Mosk. Magn. Laborat. p. 53 (1931); Ann. d. Physik **11**, 406 (1931), Fig. 3.

An Attempt to Observe a Helium Isotope

Langer[1] has recently demonstrated that Be^9 is radioactive and has suggested the possibility that He^5 might be one of the products of the disintegration and that, if so, He^5 should be found in old beryllium mineral.

Professor Gruner placed at our disposal a large crystal of beryl from the pre-Cambrian dykes of the Black Hills in South Dakota (estimated age greater than 3×10^8 years). The gases were driven out by heating the crushed crystal and were passed through a charcoal trap immersed in liquid air. A mass-spectrograph analysis of the gas not absorbed showed He^4. If He^5 was present its concentration was less than one part in 40,000 relative to He^4.

As a check on the apparatus, ordinary hydrogen was examined for the $(H^2H^1)^+$ molecular ion. An analysis of the data, taken at different pressures to correct for $(H_3^1)^+$, showed H^2 present in a concentration of the order of 1 part in 30,000 relative to H^1.

JOHN T. TATE
PHILIP T. SMITH

University of Minnesota,
April 4, 1933.

[1] R. M. Langer and R. W. Raitt, Phys. Rev. **43**, 585 (1933).

Collisions of Neutrons with Protons

With the hope of learning more about the nature of the neutron I have been studying the collisions between neutrons and protons using a Wilson cloud chamber. This work is being held up to permit the completion of some measurements on nitrogen disintegration tracks. As the progress of the two problems is very slow because of the weakness of my neutron source I have thought it advisable to make this preliminary report on the neutron-proton collisions.

Although the neutron itself leaves no track in a cloud chamber the essential facts of the collision are known if one measures the direction in which the proton is projected relative to the initial direction of motion of the neutron. I have therefore arranged a source of neutrons in a small volume surrounded by a cylinder of paraffin of diameter 12.5 mm, the whole being placed at the center of the cloud chamber. The tracks formed by the protons projected from the paraffin are photographed. Since the neutrons proceed in a radial direction the angle between the directions of motion of the neutron and of the proton may be measured.

About 150 such tracks have been measured. Corrections are applied for the volume of the paraffin effective in the

scattering and for the solid angle subtended by the chamber. To eliminate the possibility of measuring tracks due to radioactive contamination (such tracks are about as abundant as the proton tracks, but much shorter) only those which extend to the walls of the chamber are considered. On plotting the number of protons per unit solid angle projected between $\theta-5°$ and $\theta+5°$ against θ one finds a distribution curve showing a decided maximum in the forward direction and falling toward zero at 90°.

The behavior of two different models of the neutron in such collisions has been discussed theoretically by Massey.[1] He finds that both a dipole and a spherically symmetrical model should exhibit peaks around 90°, which is in disaccord with these observations. The present data seem best to fit the cosine curve which describes the scattering of elastic spheres. Massey's models seem to exhaust the proton-electron combinations so that one is tempted to regard the neutron not as a composite particle but as an elementary particle.

The details of this work will be described later in a paper to be sent to the Physical Review.

F. N. D. KURIE

Sloane Physics Laboratory,
Yale University,
April 4, 1933.

[1] H. S. W. Massey, Proc. Roy. Soc. **A138**, 460 (1932).

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CONTENTS

PHYS. REV. 43 (1933) APRIL 15

Diffuse Scattering of X-Rays from Sylvine. II. . . . . G. G. HARVEY 591

Absolute X-Ray Reflectivities of Single Crystals of Calcite, Rocksalt, Rochelle Salt and Barite . . . . PAUL KIRKPATRICK AND P. A. ROSS 596

Cathodic Disintegration of Platinum by Mercury Ions . . . . . .JOS. E. HENDERSON AND EDITH GIDEON 601

Polarizabilities of Ions from Spectra . . . . . JOSEPH E. MAYER AND MARIA GOEPPERT MAYER 605

Effects of Chemical Combination on the X-Ray Emission Spectrum of Sulphur . . . . . JOSEPH VALASEK 612

Projective Relativity and the Einstein-Mayer Unified Field Theory . . . . . BANESH HOFFMANN 615

Neutrons in the Nucleus. I . . . . . ALFRED LANDÉ 620

Neutrons in the Nucleus. II. . . . . ALFRED LANDÉ 624

Vector Model and the Pauli Principle . . . . . M. H. JOHNSON, JR. 627

Note on Almost Closed Shells . . . . . M. H. JOHNSON, JR. 632

Nuclear Magnetic Moments. . . . . .S. GOUDSMIT 636

Paschen-Back Effect of Hyperfine Structure and Polarization of Resonance Radiation. Cadmium ($6^1P_1-5^1S_0$). . . . . .N. P. HEYDENBURG 640

Notes on the Stark Effect . . . . . E. U. CONDON 648

On the Magnetization of Ferromagnetic Crystals. . . .FRANCIS BITTER 655

New Techniques in the Cosmic-Ray Field and Some of the Results Obtained With Them . . . . . ROBERT A. MILLIKAN 661

Letters to the Editor:

Secondary Absorption and Fine Structure of X-Rays as Observed with a Double Crystal Spectrometer . . . .C. D. COOKSEY AND S. T. STEPHENSON 670

Potential Energy of Diatomic Molecules . . . . . .N. ROSEN 671

On the Permeability of Iron at Ultra-Radio Frequencies . . W. ARKADIEW 671

Attempt to Observe a Helium Isotope . JOHN T. TATE AND PHILIP T. SMITH 672

Collisions of Neutrons with Protons . . . . . .F. N. D. KURIE 672

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